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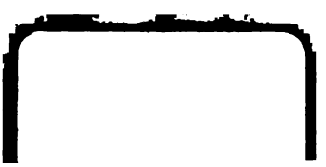

STANDARD METHODS

OF

CHEMICAL ANALYSIS

A MANUAL OF ANALYTICAL METHODS AND GENERAL REFERENCE FOR THE ANALYTICAL CHEMIST AND FOR THE ADVANCED STUDENT

EDITED BY

WILFRED W. SCOTT

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THIS BOOK IS AFFECTIONATELY DEDICATED

TO MY FATHER,

Rev. Thomas Jefferson Scott, D.D

PREFACE

THIS book is a compilation of carefully selected methods of technical analysis that have proven of practical value to the professional chemist. The subjects have been presented with sufficient detail to enable one with an elementary knowledge of analytical processes to follow the directions; on the other hand, lengthy exposition, theoretical dissertation and experimental data are purposely avoided, in order to include a large amount of information in a compact, accessible form. References to original papers are given when deemed advisable.

For methodical arrangement the material is grouped under three major divisions—Part I. Quantitative determination of the elements. Part II. Special subjects. Part III. Tables of information.

In the first division the elements are generally taken up in their alphabetical order, each chapter being fairly complete in itself, cross-references being given to certain details included elsewhere to avoid repetition. For example, the complete directions for separation of the halogens are given in the chapter on chlorine, and references to these details are given in the chapters dealing with the other members of this group. Occasionally it has been deemed advisable to place several related elements together in the same chapter.

Each chapter on the elements is generally arranged according to the following outline:

Physical Properties. Atomic weight; specific gravity; melting-point; boiling-point; oxides.

Detection. Characteristic reactions leading to the recognition of the element.

Estimation. The subject is introduced with such information as is useful to the analyst.

Preparation and Solution of the Samples. Here directions are given for the preparation and decomposition of characteristic

materials in which the element occurs. Recommendations to the best procedures are included to assist the analyst in his choice.

Separations. This section is devoted to procedures for the removal of substances, commonly occurring with the element, that may interfere with its estimation. In the absence of such substances, or in case methods are to be followed by which a direct estimation of the element may be made in the presence of these substances, this section on separations may be omitted in the course of analysis. Here the discretion of the chemist is necessary, and some knowledge of the substance examined essential.

Methods. The procedures are grouped under gravimetric and volumetric methods. Several processes are generally given to afford the opportunity of selection for particular cases and for economical reasons where special reagents may not be available.

In many of the chapters methods for determining traces of the element are given, and the subjects are concluded by typical examples of complete analysis of substances containing the elements.

The titles to the procedures generally give a clue to the processes. Names of originators are occasionally retained where common usage makes the methods generally known by these.

Although the combined acid radicals are taken up with the elements to which they may be assigned, a chapter is devoted to the more important of the acids in their free state, and is placed with the other special subjects in the second division of the book. Here are found chapters on water, paint, oil, alloys, coal, cement, gas, and such subjects as are best classed in sections apart from simple substances dealt with in the first portion of the work.

The last portion of the book is devoted to tables of the more important arithmetical operations. These are designed to assist the analyst to greater accuracy of calculations, as well as to relieve him of needless expenditure of time and energy.

The material herein included has been carefully selected, an effort having been made to obtain the more trustworthy method that will meet the general needs of technical chemists. The collaborators are aware of the limitations of analytical processes and will gladly welcome criticism of the procedures, and suggestions that will enable them to improve the work.

The editor wishes to acknowledge his indebtedness to those

cooperating with him in the compilation of this volume. The names of these appear in the table of contents, as well as on the title pages of their respective chapters. For useful suggestions and information of value to this work, or for assistance in reviewing manuscript or proof we express our appreciation of Dr. F. A. Gooch, Mr. C. W. Ferguson, Mr. W. S. Allen, Dr. Allen Rogers, Mr. L. E. Barton, Mr. T. T. Gray, Mr. W. G. Derby, Mr. A. W. Betts, Mr. N. F. Harriman, Dr. E. Bedtel, Mr. W. F. Doerflinger, Mr. J. M. Cratty, Mr. B. S. Clark and others, mention of whom is made in the text. We would make special mention of Dr. John C. Olsen for his review of the entire manuscript and for many vaulable suggestions, which are incorporated in the work. We wish to express our high appreciation of Dr. Frank E. Hale for his invaluable assistance in reviewing proof and for his contributions.

A list of the majority of publications consulted is given in alphabetical order in the appendix of this volume. Reference to these authorities will be found throughout the book.

W. W. Scott.

New York City,
January, 1917.

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Research Chemist, New York City

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Wm. F. Doerflinger

Chief Chemist, Perry-Austin Manufacturing Company

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W. L. SAVELL, Ph.D.

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WILFRED W. SCOTT

Research Chemist, General Chemical Company

WALLACE G. DERBY

Research Chemist, Nichols Copper Company

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Research Chemist, Nichols Copper Company

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WILFRED W. SCOTT

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NICKEL

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WILFRED W. SCOTT

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GAS ANALYSIS

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PART I

TECHNICAL METHODS FOR THE DETECTION AND DETERMINATION OF THE MORE IMPORTANT ELEMENTS

ALUMINUM[1]

WILFRED W. SCOTT

Al, *at.wt.* 27.1; *sp.gr.* 2.583; *m.p.* 658.7°; *b.p.* 2200°; *oxide* Al_2O_3.

DETECTION

The sample is brought into solution according to one of the procedures outlined under "Preparation and Solution of the Sample." Silica is removed by taking the solution to dryness, boiling the residue with hydrochloric acid and filtering. The members of the hydrogen sulphide group are removed as usual with H_2S, the filtrate boiled to expel the excess of H_2S, iron oxidized with nitric acid, and aluminum, iron and chromium precipitated as hydroxides by addition of ammonium hydroxide in presence of ammonium chloride. On treating the precipitate with sodium peroxide, aluminum and chromium hydroxides dissolve, whereas ferric hydroxide remains insoluble. Aluminum hydroxide is precipitated by acidifying the alkaline solution with hydrochloric or nitric acid, and neutralizing with ammonia; chromium remains in solution.

The white gelatinous precipitate of aluminum hydroxide may be confirmed by adding a drop of cobalt nitrate solution and burning the filter. The residue will be colored blue by the resulting aluminum cobalt compound.

Sodium thiosulphate, $Na_2S_2O_3$, added to a neutral or slightly acid solution, containing aluminum, precipitates aluminum hydroxide, upon boiling the solution. Sodium sulphite, or ammonium chloride added in large excess, will also cause this precipitation.

ESTIMATION

The determination of aluminum, in terms of alumina, Al_2O_3, is required in the evaluation of aluminum ores, bauxite, $Al_2O(OH)_4$; diaspore, $AlO(OH)$; alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$, etc. It is determined in the analysis of feldspar, halloysite, clays, granite, gneiss, porphyry, mica schist, slate, obsidian or pumice stone, cryolite, limestone, and in the complete analysis of a large number of mineral substances. The estimation of alumina is required in the analysis of cements, plaster, ceramic materials, aluminum salts, and is especially important in the control of processes in the manufacture of aluminum products. As a metal it is determined in commercial aluminum, and its alloys.

Preparation and Solution of the Sample

In dissolving substances containing aluminum it will be recalled that alumina, although ordinarily soluble in acids, is very difficult to dissolve when it is highly heated. It may be best dissolved, in this case, by fusion with sodium carbonate or with acid potassium sulphate, followed by an acid extraction. The metal is scarcely acted upon by nitric acid, but is readily soluble in the halogen acids and in hot concentrated sulphuric acids.

General Procedure for Ores. One gram of the finely powdered ore, taken from a representative sample, is placed in a platinum dish, 5 cc. of con-

[1] Also spelled Aluminium.

centrated sulphuric acid are added, followed by about 20 cc. of strong hydrofluoric acid. The mixture is evaporated over a steam bath as far as possible and then taken to SO_3 fumes on the hot plate (*Hood*). Upon cooling, a little dilute hydrochloric acid is added and the mixture warmed. The solution is diluted with distilled water and filtered if any residue remains.

The insoluble residue remaining on the filter may be brought into solution by fusing the ignited residue with sodium carbonate or acid potassium sulphate. If barium is present sodium carbonate fusion is made and the melt extracted with water to remove the sodium sulphate. The residual carbonates may now be dissolved with hydrochloric acid.

SULPHIDE ORES should be oxidized with nitric acid and bromine according to the general procedure for decomposing pyrites in the determination of sulphur.

The solution of the sample having been effected, aluminum is separated from elements that interfere in its estimation. Directions for the removal of these substances are given under "Separations." The element is now in solution in such form that it may be determined gravimetrically or volumetrically.

Fusion Method. Sodium Carbonate. The air-dried material, ground to a fine powder, is placed in a glass-stoppered bottle. If the determination is to be made on the dry basis, moisture is driven out by placing the material in the hot air or steam oven for an hour (100 to 110° C.). One gram sample, placed in a large platinum crucible, is mixed with 4 to 5 grams of anhydrous sodium carbonate and the material heated to fusion, the heating being continued until the molten mass appears clear. The liquid mass may be poured on a large platinum crucible lid, or if preferred, allowed to cool in the crucible, a platinum prod being held in the fusion until it solidifies. By gently heating the crucible over a flame the fusion loosens from the sides and may be lifted out on the prod. In either case the cooled mass is dissolved by placing it, together with the crucible in which the fusion was made, in a casserole, and treating with hydrochloric acid, the casserole being covered with a clock glass during the reaction.

Silica is removed by evaporating the solution to dryness on the water or steam bath and drying in the oven at 110° C. for an hour or more. The residue is extracted with hot dilute hydrochloric acid and silica filtered off.

If the solution is cloudy upon treatment of the fusion with acid, it indicates either the presence of barium sulphate or incomplete decomposition of the sample. In the latter case the residue is gritty and the fusion of this material should be repeated.

Fusion with Potassium Bisulphate. This procedure is recommended for the decomposition of commercial alumina or calcined Al_2O_3. The procedure is similar to the sodium carbonate fusion with the exception that less heat is required. A silica dish may be used, if desired, in place of platinum.

Extraction of Ores of Aluminum for Their Commercial Valuation. The available alumina in bauxite, alunite, clays and aluminum-bearing material may be approximately ascertained by digesting 5 grams of the pulverized sample with 45 cc. of 5 N. H_2SO_4 for three hours in a Kjeldahl flask with reflux condenser, the heat being so regulated [1] that the drip from the condenser amounts to 5 to 8 drops per minute. The solution filtered hot, together with the washings of the residue is diluted to 1000 cc. Aliquot portions of this solution

[1] Method for controlling temperature by observing condensation suggested by W. S. Allen.

are taken for determination of the desired soluble constituents, according to the procedures outlined under bauxite analysis in the latter portion of the chapter.

Solution of Metallic Aluminum and its Alloys. The metal may be dissolved in dilute hydrochloric acid, 1 : 1, or in a solution of sodium hydroxide or potassium hydroxide.

Alloys of aluminum are best brought into solution with a mixture of hydrochloric and nitric acids.

SEPARATIONS

General Considerations. In the usual course of analysis, aluminum is in solution as a sulphate or as a chloride, silica having been removed by dehydration, as described under "Preparation and Solution of the Sample." The following interfering elements may be present in the solution: iron, manganese, arsenic, antimony, titanium, phosphoric acid, and more rarely chromium and zirconium. In alloys of aluminum other elements may be added to this list. The separation more commonly required is from iron, aluminum and iron being precipitated together as the hydroxides. In usual practice the two are weighed together as Fe_2O_3 and Al_2O_3, after ignition to this form, and iron then determined, either on a separate portion of the sample, or by solution of the precipitate by fusion with sodium carbonate or potassium bisulphate and subsequent extraction with hydrochloric acid. The following procedures of separations are given for special cases less commonly required in analysis. The chemist should be familiar with the substance with which he is working and have a general idea of its composition in order to be able to choose the correct procedure for estimation of the aluminum content. In ores and materials to be used for production of aluminum compounds the results are reported in terms of the oxide-alumina, Al_2O_3, in alloys as the element, Al.

Removal of Silica. This compound has already been considered under "Preparation and Solution of the Sample," SiO_2 being removed by taking the solution to dryness, dehydrating the oxide by additional heating in the oven, followed by extraction of the soluble constituents with dilute hydrochloric acid and filtration. Under the first procedure for solution of the ore by sulphuric and hydrofluoric acids silica is expelled as gaseous SiF_4.

Separation from Iron. 1. Aluminum hydroxide is precipitated by the addition of a salt of a weak acid to its neutral or slightly acid solution, iron remaining in solution. Details of the procedure for precipitation of aluminum hydroxide by means of sodium thiosulphate are given under "Gravimetric Methods for Determination of Aluminum," page 9.

2. Aluminum chloride is precipitated from a concentrated solution of hydrochloric acid and ether saturated with HCl gas. Details of the procedure are given under the gravimetric methods for aluminum, page 10.

NOTE. The following additional procedures for separation of iron and alumina have been suggested:

(*a*) Precipitation of iron as FeS in presence of organic acids, citric, tartaric, salicylic, etc., aluminum remaining in solution.

(*b*) Precipitating iron by adding sodium peroxide to a cold neutral solution of the elements until the precipitate first formed dissolves, then decomposing the sodium ferrate by boiling, $Fe(OH)_3$ precipitates, Al remaining in solution. (Glaser, J. S. C. I., 1897, 936.)

(*c*) The neutral solution of the elements is boiled with freshly precipitated MnO_2, which causes the precipitation of iron as $Fe(OH)_3$, while aluminum remains in solution, (chromium also passes into the filtrate).

(*d*) Precipitation of iron from acid solutions by means of amino-nitrosophenylhydroxylamine, (cupferron), aluminum remaining in solution. (O. Baudisch, Chem. Ztg., **33**, 1298, 1905. *Ibid.*, **35**, 913, 1911; O. Baudisch and V. L. King, J. I. E. C., 3, 627, 1911).

(*e*) Precipitation of aluminum (together with phosphoric acid, if present), by phenylhydrazine, added to the reduced, weakly acid or neutral solutions. Iron, cobalt, nickel, calcium, and magnesium remain in solution. (Hess and Campbell. C. N., lxxxi, 158. Engles, J. S. C. I., 1898, 796.)

(*f*) Electrolytic separation of iron by amalgamation with mercury cathode and determining aluminum in the solution. (Kretzschmar, J. S. C. I., 1890, 1064; Kolin and Woodgate, J. S. C. I., 1889, 260.)

Phosphoric Acid. In presence of phosphoric acid, the phosphates of iron and alumina together with the phosphates of the other elements of the group and those of the alkaline earths will be precipitated upon making the solution alkaline with ammonia. Should iron and alumina be the only elements of these two groups present in the solution, they may be precipitated together as phosphates, iron determined by titration and calculated to the phosphate salt, and alumina obtained by difference. Occasionally, however, it is necessary to remove phosphoric acid.

Removal of Phosphoric Acid. The material is fused with about six times its weight of a mixture of 4 parts Na_2CO_3 and 1 part SiO_2 (silex), and the melt extracted with water containing ammonium carbonate. Iron and aluminum remain on the filter, upon filtration, while sodium phosphate passes into solution. Both the precipitate and filtrate contain silica. The precipitate of iron and alumina is dissolved in hydrochloric acid and taken to dryness, the residue dehydrated as usual, then treated with dilute hydrochloric acid and silica filtered off. The solution contains iron and aluminum in form of chlorides

Separation of Aluminum from Chromium. The solution is made strongly alkaline with sodium or potassium hydroxides and chromium oxidized by passing in chlorine gas or by adding bromine. The solution is now acidified with nitric acid and aluminum hydroxide precipitated by addition of ammonium hydroxide, chromium remaining in solution as a chromate.

Separation of Aluminum from Manganese, Cobalt, Nickel, Zinc, the Alkaline Earths, and Alkalies. Iron and aluminum are precipitated as basic acetates, the other elements passing into solution. Details of the procedure are given under the basic acetate method on page 260.

In absence of phosphates, these elements do not interfere in the determination of aluminum by precipitation as the hydroxide.

Separation of Aluminum from Titanium. Details of the procedure are given under "Titanium."

Separation of Aluminum from Uranium. Aluminum is precipitated as a carbonate in presence of a large amount of ammonium salts by addition of a large excess of ammonium carbonate and ammonium sulphide, while uranium remains in solution as the complex compound $UO_2(CO_3)_3(NH_4)_4$.

Separation from Glucinum. Aluminum is soluble in the fixed alkalies and remains in solution on boiling; glucinum also dissolves, but is precipitated on boiling. Glucinum is soluble in an excess of ammonium carbonate, aluminum is not.

For additional separations see chapter on element in question.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

There are two general procedures for the gravimetric determination of aluminum. *A.* Direct determination, when it is possible to precipitate the hydroxide or phosphate of the element, free from impurities. *B.* Indirect determination when the element is precipitated and weighed along with iron, the latter then determined by titration and aluminum estimated by difference.

Determination by Hydrolysis of an Aluminum Salt with Ammonium Hydroxide

Principle. The method depends upon the hydrolysis of a soluble salt of aluminum by neutralizing the free and combined acid with ammonia. This hydrolysis takes place in presence of the small amount of free acid that results by dissociation of ammonium chloride, $NH_4Cl+H_2O=NH_4OH+HCl$, which is sufficient to prevent precipitation of magnesium. The direct determination of aluminum by this procedure excludes the presence of elements undergoing hydrolysis with similar conditions. Iron, chromium, titanium, zirconium, thallium, cerium interfere. In their presence a separation must be made.

Reaction. $AlCl_3+3NH_4OH=Al(OH)_3+3NH_4Cl$.

If phosphoric acid is present in the solution aluminum will be precipitated as the phosphate, $AlPO_4$.

Procedure. To the solution, containing aluminum, free from phosphoric acid and the elements precipitated by ammonium hydroxide, are added 10 cc. of ammonium chloride (10%) and 5 cc. of concentrated nitric acid. The solution is diluted to about 150 cc. and heated to boiling. Upon cooling slightly, carbonate-free ammonium hydroxide is added slowly from a burette until a slight permanent precipitate forms, and then drop by drop until the solution reacts alkaline to litmus paper and the odor of ammonia is faintly perceptible. The precipitate is allowed to settle on the water bath for a few minutes, then filtered hot and washed first several times by decantation and finally on the filter with a hot solution of ammonium nitrate. (Twenty cc. strong nitric acid diluted and neutralized with ammonium hydroxide and made to 1000 cc.)

The precipitate is purified, if other members of the ammonium sulphide group and following groups are present, as the gelatinous precipitate is apt to occlude some of these. This is accomplished by dissolving the precipitate in a small amount of hot, dilute hydrochloric acid, 1 : 1, the solution being caught in the beaker in which the first precipitation was made. The precipitation of the hydroxide is repeated exactly as is stated above. The precipitate, washed free of chlorides ($AgNO_3$ test), is drained of water and placed together with the filter paper in a platinum crucible.

The ignition of the precipitate is conducted slowly at first until the paper is thoroughly charred, the heat is now increased to the full power of the Meker blast, the crucible being covered to prevent mechanical loss. Blasting for thirty minutes is generally sufficient to dehydrate the oxide, Al_2O_3. It is advisable, however, to repeat the heating until the weight becomes constant. The residue is weighed as Al_2O_3.

$$Al_2O_3 \times 0.5303 = Al.$$

NOTES. Ammonia should be free from carbonates. Upon long standing with frequent exposure to air the ammonia takes up CO_2, forming carbonate of ammonia. Freshly distilled ammonia will be pure, the carbonate being precipitated by addition of lime in the distilling flask. Ammonia is best kept in a ceresine or paraffine bottle. It will then remain free from silica, which it invariably contains when confined in glass bottles.

Long heating of the mixture containing the aluminum precipitate is objectionable.

1. The solution is apt to become acid owing to the decomposition of ammonium salts and the volatilization of ammonia.

2. The precipitate will become slimy and will be difficult to wash and filter. It is preferable to redissolve and again precipitate if this condition occurs.

3. The CO_2 of the air is apt to be absorbed by the solution, causing the precipitation of calcium carbonate, etc., should the solution be exposed for any length of time.

4. Silica from the beaker will contaminate the precipitate.

Hence it is advisable to filter as soon as possible after making the precipitation of $Al(OH)_3$.

S. and S. No. 589, black band filter paper filters well and may be used to advantage with precipitates of the nature of aluminum hydroxide. B. and A. No. B. filter is also good.

Washing the precipitate with ammonium nitrate prevents the aluminum from passing through the filter and keeps it from packing. It favors the formation of the insoluble hydrogel form of the hydrate while preventing the formation of the soluble hydrosol. Ammonium chloride may be used in place of nitrate.[1]

Aluminum hydroxide is soluble in acids and alkalies. The ignited oxide, Al_2O_3, is insoluble in acetic acid but is soluble in mineral acids and the fixed alkalies, It is rendered very difficultly soluble in acids by strong ignition, generally requiring fusion with sodium carbonate or potassium bisulphate with subsequent acid treatment to effect solution.

Al_2O_3, *m.w.*, 102.2; *sp.gr.*, 3.73 to 3.99; *m.p.*, 2020° C.

A yellow or reddish precipitate indicates the presence of iron, an element frequently present with aluminum. Should this be the case, iron must be determined, either in a separate portion of the sample, or in the residue obtained by the procedure outlined. The amount of Fe_2O_3 is subtracted from the total residue and Al_2O_3 obtained by difference.

If ***phosphoric acid*** is present the phosphate of alumina will precipitate together with the phosphates of elements insoluble in alkaline solutions. Should phosphoric acid be present either its removal is essential, or the phosphate method for alumina should be followed.

Fluorides hinder the precipitation of aluminum.[2] Evaporation to dryness and heating the residue to redness will transform fluorides to oxides and overcome this difficulty.

Sulphates tends to hold up aluminum from precipitation and a certain amount of sulphuric acid is occluded by the aluminum hydroxide precipitate. Magnesium is more apt to precipitate with alumina in presence of sulphates.[3] Ammonium chloride greatly lessens this difficulty.

Traces of alumina may be recovered from the filtrate by evaporation to dryness, ignition and resolution with HCl. The $Al(OH)_3$ is now precipitated with NH_4OH.

Since alumina absorbs moisture from the air, the crucible containing this compound should be kept covered in a desiccator[3] until weighed. Ignited alumina is strongly hygroscopic.

[1] W. Blum, Jour. Am. Chem. Soc., **38**, 7, 1282, 1916. C. F. Sidener and Earl Pettijohn, Jour. Ind. Eng. Chem., **8**, 8, 714, Aug., 1916.

[2] E. P. Veitch, Jour. Am. Chem. Soc., **22**, 246, 1900. W. R. Bloor, ibid., **29**, 1603, 1907. L. P. Curtman and H. Dubin, ibid., **34**, 1485, 1912.

[3] L. F. J. Wrinkle, C.N., **22**, 4, 1870.

Determination of Aluminum by Hydrolysis, Neutralizing the Mineral Acid by Addition of a Salt of a Weak Acid. Sodium Thiosulphate Method [1]

If a salt of a weak acid and strong base is added to a neutral or slightly acid solution of an aluminum salt containing a mineral acid, transposition takes place and aluminum is hydrolyzed.

Reaction. $2AlCl_3+3Na_2S_2O_3=6NaCl+Al_2(S_2O_3)_3$

and $Al_2(S_2O_3)_3+3H_2O=2Al(OH)_3+3SO_2+3S.$

Procedure. If the solution is acid, dilute ammonia is added until a precipitate forms that dissolves with difficulty, but not enough ammonium hydroxide to cause a permanent precipitation. The solution is diluted so that it contains about 0.1 g. Al per 200 cc., then an excess of sodium thiosulphate is added, and the solution is boiled free of SO_2. $Al(OH)_3$ precipitates along with free sulphur. If iron is absent it is advisable to add a few drops of ammonium hydroxide until the solution has a slight odor of ammonia. The mixture again boiled is filtered and the residue of $Al(OH)_3$ and sulphur washed with hot water containing ammonium chloride or nitrate. The precipitate is dried, separated from the filter, the latter ignited and the ash added to the main precipitate. Alumina is now determined by blasting to constant weight, the residue being weighed as Al_2O_3.

NOTES. The above method may be employed for separation of aluminum from iron, the addition of ammonia, following the neutralization of the mineral acid by thiosulphate being omitted. The precipitation of $Al(OH)_3$ by this procedure gives a more dense and better filtering precipitate than does ammonia alone.

NOTE. G. Wynkoop and E. Schirm [2] use sodium nitrite as the salt of a weak acid for neutralizing the mineral acid.

Reaction. $2AlCl_3+6HOH=2Al(OH)_3+6HCl$ and

$$6HCl+6NaNO_2=6NaCl+3H_2O+3NO+3NO_2.$$

Precipitation of Aluminum as a Phosphate

Principle. This procedure, developed by Carnot,[3] is of special value in determination of aluminum in iron and steel. It is founded on the reaction that aluminum is precipitated as the neutral phosphate, from a boiling solution faintly acid with acetic acid. Iron, reduced to the ferrous condition by addition of sodium hyposulphite, does not interfere.

Procedure. A sample of 10 grams of iron or steel, in a platinum dish, covered with a piece of platinum foil, is dissolved by addition of hydrochloric acid. The solution is diluted to about 100 cc. and filtered into a flask, the residue of carbon, silica, etc., is washed thoroughly and the filtrate is neutralized by addition of ammonium hydroxide and ammonium carbonate; no permanent precipitate should form. A little sodium hyposulphite is added, and when

[1] Method by Chancel, Compt. rend., **46**, 987. Z. anal. Chem., **3**, 391.
[2] J. Am. Ch. Soc., **19**, 434 (1897).
[3] A. Carnot, Moniteur Scientifique, 1891, p. 14.

the liquid, at first violet, becomes colorless, 2 or 3 cc. of a saturated solution of sodium phosphate and 5 or 6 grams of sodium acetate, dissolved in a little water, are added. The solution is boiled until free of sulphurous acid odor (about three-quarters of an hour). The solution is filtered off from the precipitated aluminum phosphate (mixed with a little silica and ferric phosphate) and washed with boiling water. The precipitate on the filter is treated with hot dilute hydrochloric acid the filtrate caught in a platinum dish, and then evaporated to dryness and heated at 110° C. for an hour to dehydrate silica. The residue is taken up with dilute hydrochloric acid and the solution filtered free of silica. Upon dilution to about 100 cc. with cold water, the solution is neutralized as before, a little hyposulphite is added to the cold solution and then a mixture of 2 grams of sodium hyposulphite and 2 grams of sodium acetate. The material is boiled for half an hour or more, filtered and the aluminum phosphate residue washed with hot water, then dried, ignited and weighed as aluminum phosphate. The residue contains 22.19% Al.

$$AlPO_4 \times 0.2219 = Al. \quad AlPO_4 \times 0.4185 = Al_2O_3.$$

NOTE. Properties of $AlPO_4$, *m.w.*, 122.14; *sp.gr.*, 2.59; infusible, insoluble, in H_2O and in $HC_2H_3O_2$, soluble in mineral acids and in alkalies; white, amorphous salt.

Precipitation of Aluminum as Aluminum Chloride[1]

Principle. Gooch and Havens found that aluminum chloride is practically insoluble in a mixture of concentrated hydrochloric acid and ether saturated with HCl gas, 5 parts of $AlCl_3.6H_2O$ equivalent to 1 part of Al_2O_3 dissolving in 125,000 parts of the mixture. The method serves for a separation of aluminum from iron, berillium, zinc, copper, mercury and bismuth, the chlorides of these elements being soluble under the above conditions. Barium, however, is precipitated as a chloride with aluminum, if it is present in the solution.

Procedure. To the concentrated aqueous solution of aluminum is added a convenient volume of strong hydrochloric acid (15 to 25 cc.) and an equal volume of ether. The mixture is best placed in a large platinum crucible which is kept cool in running water. HCl gas is passed into the solution to saturation. The precipitated chloride of aluminum is filtered upon asbestos in a weighed Gooch crucible and then washed with a mixture of ether and water 1 : 1, saturated with HCl gas. The precipitate is dried for half an hour at 150° C., then covered with a layer of C.P. mercuric oxide (1 gram) and heated at first gently over a low flame (hood) and then blasted to constant weight. The residue is weighed as Al_2O_3.

NOTES. HCl gas is generated by dropping strong sulphuric acid into concentrated hydrochloric acid according to the procedure described under the determination of arsenic by volatilization as arsenious chloride. The gas may be produced in a Kipp generator by the action of concentrated sulphuric acid on ammonium chloride.

The filtrate from aluminum contains iron, berillium, copper, zinc, etc., if these are present in the original solution. If much iron is present it is necessary to increase the amount of ether to prevent precipitation of the ferric salt.

[1] F. A. Gooch and F. S. Havens, Am. Jour. Sci. (4), **11**, 416.

VOLUMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

Volumetric Determination of Combined Alumina in Aluminum Sulphate and Aluminum Salts

Introduction. Aluminum salts dissociate in hot solutions and react acid to phenolphthalein indicator; the acid readily combines with fixed alkalies, forming the neutral alkali salt. The end point of the reaction is indicated by the pink color produced upon phenolphthalein by the excess of alkali. From the amount of caustic required the percentage of combined Al_2O_3 may be calculated. The following reaction takes place:

$$Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3 + 3Na_2SO_4.$$

Procedure. The factor weight,[1] 3.4067 grams, is dissolved in a 4-in. casserole with 100 cc. of distilled water, 1 cc. of phenolphthalein indicator added, and the sample titrated boiling hot[2] with N/2 NaOH, added from a chamber burette, graduated from 50 to 100 cc. in tenths of a cc.[1] The solution is kept boiling during the titration and is constantly stirred. Towards the end of the reaction the alkali is added cautiously drop by drop until a permanent pink color is obtained.

Cc. of NaOH required divided by 4 = per cent combined Al_2O_3.[3]

Combined Al_2O_3 + free Al_2O_3 = total Al_2O_3.

NOTES. If iron is present a correction must be made for it after determining the ferrous and ferric forms as given below.

The amount of phenolphthalein indicator used should be the same in each determination. An excess of indicator causes low results. It has been noted in case of alums where iron does not interfere that best results are obtained with three or four drops of phenolphthalein solution. Iron tends to mask the end point, hence a larger amount of indicator is necessary if this is present.

Correction for Iron if Present. Since iron salts will also dissociate and titrate with aluminum salts, by this method a correction has to be made for iron if present. Total Al_2O_3 in presence of iron =

combined $Al_2O_3 - (FeO \times .47 + Fe_2O_3 \times .64)$ + basic Al_2O_3 + an additive factor.

The additive factor is obtained by subtracting

(Combined Al_2O_3 + basic Al_2O_3) $- (FeO \times .47 + Fe_2O_3 \times .64)$ volumetric,

from total Al_2O_3 obtained by gravimetric analysis of an average sample.

[1] Large samples must be taken for salts containing less than 13 per cent Al_2O_3 if the chamber burette is to be used. E.g., potash alum twice this amount is advisable.

[2] Otto Schmatolla, Berichte, xxxviii, No. 4. C. N., 91–2375–236 (1905).

[3] If free acid is present (see next method), the equivalent volume in terms of $\frac{1}{2}$ N acid must be deducted from the total titration for combined alumina before dividing by 4.

Ferrous Iron, Ferric Iron, and Total Iron. A five-gram sample is dissolved in water and the iron oxidized with a few drops of strong potassium permanganate solution; the solution should be pink; the excess of permanganate is destroyed by a drop or so of normal oxalic acid solution and the total iron determined by stannous chloride solution method for iron. On a separate sample ferric iron is determined. Ten grams of the sample are dissolved in an Erlenmeyer flask by boiling with hydrochloric acid, 2 : 1, in an atmosphere of CO_2 to prevent oxidation, and the iron titrated with standard stannous chloride. The difference between total iron as Fe_2O_3 and ferric oxide = ferrous iron in terms of Fe_2O_3. This multiplied by .9 = FeO.

Combined Sulphuric Acid

Provided no free acid is present, the per cent combined sulphuric acid in aluminum sulphate is obtained by multiplying the cc. caustic titration for total alumina by 0.72.

In case free acid is present, the per cent free acid deducted from total acid found by titration gives combined acid.

Sulphuric acid combined with the fixed alkalies is not titrated.

Determination of Free Alumina or Free Acid by the Potassium Fluoride Method

Introduction. The method suggested by T. J. I. Craig (J. S. C. I. **30**, 185), has been modified by the author,[1] after a personal investigation of the details involved. In this modified form it has been used successfully as a rapid works method. Frequent gravimetric checks on a large number of determinations have shown it to be accurate.

The procedure is based upon the fact that an excess of neutral potassium fluoride decomposes aluminum salts, forming two stable compounds, which react neutral to phenolphthalein, while the free acid remains unaltered, the following reaction taking place:

$$Al_2(SO_4)_3 + 12KF + xH_2SO_4 = 2AlF_3 3KF + 3K_2SO_4 + xH_2SO_4.$$

The precipitate $AlF_3 3KF$ is insoluble in an excess of the potassium fluoride reagent and is not appreciably attacked by acids or alkalies. Although theoretically about 7 parts by weight of potassium fluoride is sufficient to combine with 1 part of aluminum sulphate, in practice it is advisable to use twice this amount.

Reagents Required. ***Half Normal*** solutions of sulphuric acid and potassium hydroxide. (sodium hydroxide may be used.)

Phenolphthalein indicator, 0.1% alcoholic solution.

Potassium fluoride solution; made by dissolving 1000 grams of potassium fluoride in about 1200 cc. of hot, CO_2-free water, then neutralizing the solution with hydrofluoric acid or potassium hydroxide as the reagent may require, using 5 cc. of phenolphthalein as indicator. Dilute sulphuric acid may be used in place of hydrofluoric acid in the final acid adjustment to get a neutral product. One cc. of the solution in 10 cc. of CO_2-free water should appear a faint pink. The concentrated mix is filtered if necessary and then diluted to 2000 cc. with CO_2-free water. The gravity will now be approximately 1.32 or about 35° Bé. One cc. contains 0.5 g. potassium fluoride.

[1] W. W. Scott.

Method of Procedure

Solids. 3.4067 g. of the finely ground sample, or an equivalent amount in solution (100 cc. of sample containing 34.067 g. per liter), are taken for analysis The powder is dissolved by boiling with 100 cc. of distilled water in a 4-in. casserole with clock glass cover. To the hot solution 10 cc. of N/2 H_2SO_4 are added and after cooling to room temperature, 20° C., 18 to 20 cc. of the potassium fluoride reagent are added and 0.5 cc. of phenolphthalein. The solution is now titrated with N/2 KOH, added drop by drop until a delicate pink color, persisting for one minute, is obtained. This titration shows whether the product is basic or acid.

Basic Alumina. This is indicated when the alkali back-titration is less than the amount of acid added. Free Al_2O_3 = (cc. H_2SO_4 − cc. KOH) ÷ 4.

Free Acid. In case the back-titration of the alkali is greater than the cc. of acid added, free acid is present. Free acid = (cc. KOH − cc. H_2SO_4) × 0.72.

Liquors. In works control it is necessary to test the concentrated liquors to ascertain whether these are basic or acidic. The Bé. or sp.gr. of the solution having been taken, 5 cc. is diluted to 100 cc. with distilled, CO_2-free water. If H_2S is present, it is expelled by boiling the solution, which should be acid, 10 cc. of N/2 H_2SO_4 is added, the solution cooled, and KF and phenolphthalein added and the titration made as in case of solids.

If basic (cc. H_2SO_4 − cc. KOH) × (.0245 × .3473 × 100) ÷ (5 × sp.gr.) = Al_2O_3.

If acid (cc. KOH − cc. H_2SO_4 × 2.45) ÷ wt. of sample = per cent free acid (H_2SO_4).

If neutral, the back titration of the alkali is the same as the cc. acid added.

NOTES. CO_2-free water must always be used when phenolphthalein indicator is necessary. This may be obtained by boiling distilled water for several minutes to expel CO_2. This reagent is very sensitive to carbonic acid.

If the sample does not dissolve clear, a prolonged digestion with previous addition of the required amount of standard acid, 10 cc., is advisable. This is best accomplished in an Earlnmeyer flask with a return condenser.

Darkening of the solution during the back titration with the alkali, indicates that an insufficient amount of fluoride has been added. If this is the case it will be necessary to make a fresh determination.

The fluoride method has the following advantages. Determinations may be made by gas or electric light. The end point is easily detected. No neutral standard is necessary as in case of the tint method.

Ammonium salts, if present, must be expelled by boiling the sample with an excess of standard KOH and this excess determined.

3.4067 = 2.45225 × .3473 × 4 (i.e. gms. H_2SO_4 per 100 cc. N/2 acid multiplied by 4 times factor to equivalent Al_2O_3). Derived directly from mol. wt. of Al_2O_3 = (.1022 × 100 × 4) ÷ (6 × 2). 0.72 = 2.8792 ÷ 4 (i.e. factor Al_2O_3 to H_2SO_4 + 4).

The main details of the above volumetric procedures were worked out at the Laurel Hill Laboratory, General Chemical Company, and are published by courtesy of this company.

The author is indebted to Mr. W. S. Allen for his criticism and valuable suggestions in the volumetric procedures for determining alumina.]

Detection and Colorimetric Estimation of Minute Amounts of Aluminum with Alizarin S.—Atack's Method [1]

The reagent used is a 0.1% filtered solution of commercial alizarin S, the sodium salt of alizarin monosulphonic acid (yellow with acids, purple with alkalies).

Test. To 5 cc. of the neutral or acid solution under examination is added 1 cc. of the reagent, and then ammonia until the solution is alkaline, as shown by the purple color. The solution is boiled for a few moments, allowed to cool, and then acidified with dilute acetic acid, when red coloration or precipitate remaining is conclusive evidence of the presence of aluminum. The red calcium, strontium, barium, zinc and magnesium salts, and salts of other metals later than Group II are readily soluble in cold dilute acetic acid, and do not interefere with the coloration.

Phosphates or chromium do not interfere and comparatively large amounts of iron may be present (0.003 milligram Al in presence of 1 milligram ferric iron, 10 milligrams chromium salt). In presence of greater quantities of iron citric acid is added to keep this in solution.

Delicacy of the Test. One part of aluminum may be detected in 10 million parts of water.

Quantitative Estimation, Colorimetric

Procedure. The original solution (5 to 20 cc.) is acidified with hydrochloric or sulphuric acid. Ten cc. of glycerin and 5 cc. of a 1% solution of alizarin S are added, the solution made up to about 40 cc. with water (in presence of much iron or chromium citric acid is added to form the double citrates) and then rendered slightly ammoniacal. After standing for five minutes, the cold solution is acidified with dilute acetic acid, the alizarin S acting as indicator (red coloration) until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard. Suitable amounts of aluminum for estimation are 0.005 to 0.05 milligrams, the solution under examination being suitably diluted if necessary.

BAUXITE ANALYSIS [2]

Characteristic bauxites.....	H_2O	SiO_2	Fe_2O_3	Al_2O_3	TiO_2
Arkansas.....		6.4%	1.43%	87.3%	3.99%
Georgia.....	36%	9-15	1-14	42-62	1.8-2.3
Tennessee.....	27.6	18.4	4.1	49.9	

The bauxite received in cars is sampled during the unloading
he standard procedure for ores. If the sample is a composite
the total weights are taken and mixed, e.g., suppose three car
ctively 23,000, 32,500, and 26,340 pounds, then the aliquot

[1], Jour. Soc. Chem. Ind.; 34, 936 (1915); C. A. 9; 23; 3186 (1915).

[2] the only ore of aluminum of commercial importance. Pure alumina
o valuable for commercial use. Clay, the most abundant of alumina
nces, may eventually be used as a source for aluminum, but, by th
ds of extraction, the alumina from clay is not commercially available.

would be 23, 32.5 and 26.34 pounds, which mixed, would make a representative sample of the shipment. The ore is broken down, quartered, ground down and again quartered. The moisture is determined on 1000 grams, dried in the oven at 100° C. for one hour, the sample being spread out on a sheet of manilla paper. The dried sample is placed in a large bottle for analysis.

Procedure for Evaluation of the Ore. A method for obtaining in solution the available alumina and soluble constituents of bauxite has been given under Preparation and Solution of the Sample.

Insoluble Residue. The residue on the filter paper is ignited in a platinum dish over a low flame until the paper chars, and then over a good Meker blast for 15 to 20 minutes.

Weight of the residue × 20 = per cent insoluble residue.

Soluble Alumina. 100 cc. of the above solution (0.5 g.) is diluted with an equal volume of water, 10 cc. of hydrochloric and 2 cc. of nitric acids added and the solution boiled. Iron and alumina are now precipitated and determined in the usual way.

Soluble Iron. 200 cc. of the solution (1.0 g.), is oxidized by adding a few crystals of potassium chlorate and the solution taken to dryness. The residue is taken up with 10 to 15 cc. of concentrated hydrochloric acid and again evaporated to dryness to expel chlorine. Then taken up with 25 cc. hydrochloric acid and the iron determined by titration. The stannous chloride method is used for samples containing less than 5% iron and the dichromate method for ores containing over 5%.

Determination of Total Silica, Titanium Oxide, Ferric Oxide and Alumina

The method by the Aluminum Company of America is to digest 1 gram of the dried bauxite in 90 cc. of an acid mixture containing 12 parts of dilute sulphuric acid, 1 : 3, together with 6 parts of strong hydrochloric acid and 2 parts of nitric by volume, to this are added 10 cc. of concentrated sulphuric acid. The mixture is heated until sulphuric acid fumes are evolved, then diluted with water and filtered.

Silica. The residue is ignited and the ash fused with potassium bisulphate. The cooled fusion is taken up with 5 cc. sulphuric acid and 20 cc. of water and digested until only a white residue remains. This filtered off, washed and ignited = SiO_2.

Titanium Oxide. This is best determined colorometrically on a 0.1 gram sample according to the procedure outlined in the chapter on Titanium.

Iron and Alumina. These are determined by the usual procedure;—oxidation with potassium chlorate, precipitation with ammonium hydroxide and ignition. Iron may be determined in a separate sample (100 cc. = 0.5 g.) by titration. Al_2O_3 = difference between weighed oxides and Fe_2O_3, after subtracting TiO_2 if present.

DETERMINATION OF ALUMINUM IN IRON AND STEEL[1]

The method is especially adapted for determination of aluminum in iron and steel, but may be extended to iron ores and materials high in iron.

Procedure. Solution. Ten grams of iron or steel are dissolved by adding about 50 cc. of hot hydrochloric acid, 1 : 1, preferably in a platinum dish, covered with a platinum foil.

Precipitation. When the solution of iron is complete, it is diluted to about 100 cc. and filtered free of carbon, silica, etc. Two grams of sodium phosphate are added and the solution neutralized with ammonium hydroxide or carbonate, then cleared by hydrochloric acid with about 1 cc. excess. Twenty cc. of acetic acid are now added and the solution diluted to 300 to 400 cc. with hot water and, on boiling, 10 grams of sodium thiosulphate added. The solution is boiled free of sulphurous acid, (no odor of SO_2) about 20 to 30 minutes being necessary. The phosphate is filtered off and washed with hot water. It is again dissolved in a little hydrochloric acid and aluminum reprecipitated by neutralizing with ammonium hydroxide and adding about 1 gram of sodium phosphate together with 10 grams of sodium thiosulphate, following the above procedure. The precipitate will now be free of iron.

Ignition and Calculation. The precipitate and filter are ignited wet, first over a low flame, then gradually increasing the heat to full blast of a Meker burner. The residue contains 22.19% Al or 41.85% of Al_2O_3.

Factor $AlPO_4$ to Al = .2219.

Factor $AlPO_4$ to Al_2O_3 = .4185.

NOTES. Interfering substances. Copper may be removed by H_2S. Other members of this group will also be eliminated.

Manganese and nickel are eliminated together with small amounts of iron at the second precipitation.

Titanium may be estimation colorimetrically or separated from alumina.

Vanadium, if present, may be separated according to directions given in the chapter on Vanadium.

Chromium is eliminated by fusion of the mixed phosphates with Na_2CO_3, extraction with water, and precipitation of aluminum phosphate by adding ammonium acetate and sodium phosphate. Chromium remains in solution.

ANALYSIS OF METALLIC ALUMINUM[2]

Determination of Silicon

Acid Mixture: 400 cc. conc. nitric acid. 1200 cc. conc. hydrochloric acid. 600 cc. conc. sulphuric acid. 1800 cc. water.

Fusion Method

Dissolve 1 gram of well mixed drillings in 35 cc. of acid mixture using a 4½-inch porcelain dish with a 5-inch cover glass. When the drillings are completely dissolved, evaporate the solution not only to fuming but to complet

[1] Arnold and Ibbotson, "Steel Works Materials." Stillman, "Engineering Chemistry." "A Rapid Method for the Determination of Aluminum in Iron and Steel, C. N., 61, 313. "On the Determination of Minute Quantities of Al in Iron an Steel," J. E. Stead, J. S. C. I., 1889, 956.

[2] Standard Method of Analysis of the Aluminum Company of America. B courtesy of Mr. E. Blough, Chief Chemist.

dryness, and bake. This insures the freedom of the solution from hydrochloric and nitric acids, and the complete dehydration of the silica. Take up the residue with 10 cc. 25 per cent sulphuric acid and about 100 cc. of water; boil to complete solution of the sulphate, filter, wash well and ignite. Fuse the residue with eight to ten times its weight of sodium carbonate and take up the fused mass in a porcelain dish with sulphuric acid (1 : 1). Evaporate the resulting solution until copious fumes are evolved, which will cause the separation of the silica; dilute carefully, boil, filter, wash well and ignite in a platinum crucible and weigh. Treat the ash with hydrofluoric acid and a few drops of sulphuric acid; carefully ignite and weigh. The difference in the two weights obtained above represents the silicon as silica.

Calculate the silica to silicon by the factor 0.4693.

Graphitic Silicon

Aluminum, sometimes if not always, contains some silicon in the graphitic state; this graphitic silicon does not oxidize to SiO_2 on ignition and is not volatile with HF, which two characteristics distinguish it from amorphous silicon.

To determine graphitic silicon the mixture of Si and SiO_2 obtained as in the solution method is treated in a weighed platinum crucible with 2–3 drops of H_2SO_4 and 2–3 cc. HF.

The brown residue of Si remaining is strongly ignited and weighed; the silicon remaining is that which was in the metal in the graphitic state.

Determination of Iron

Permanganate Method

Cool the filtrate obtained from solution of the sample in acid mixture (see page 16) and reduce the iron present by passing the solution through a Jones reductor. Titrate immediately with a solution of potassium permanganate of such strength that 1 cc. equals 0.0010 gram iron.

In all cases the precautions given for use of the Jones reductor should be observed, and explicit directions given in the chapter on Iron, carefully followed. A blank determination is made by carrying out a regular iron determination with the metal sample omitted. The amount of potassium permanganate required to give the blank a distinct color is subtracted from the amount required to give the same color to each reduced solution.

The author acknowledges his indebtedness to Mr. W. S. Allen, Mr. J. P. Kelly and Dr. F. E. Hale for review and criticism of the subject.

ANTIMONY

WILFRED W. SCOTT

Sb_2 *at.wt.* 120.2; *sp.gr.* 6.62[1]; *m.p.* 630°C[2]; *b.p.* 1440°C[1]; *oxides*, Sb_2O_3, Sb_2O_4, Sb_2O_5.

DETECTION

Hydrogen Sulphide precipitates the orange-colored sulphide of antimony from fairly strong hydrochloric acid solutions (1 : 4) in which several members of the group remain dissolved. Arsenic is also precipitated. The latter may be removed by boiling the solution containing the trichloride, $AsCl_3$ being volatile.

If antimony is already present as a sulphide, together with other elements of the hydrogen sulphide group, it may be dissolved out by treating the precipitate with sodium hydroxide, potassium hydroxide, sodium sulphide, ammonium polysulphide in solution. Antimony sulphide is reprecipitated upon acidifying the filtrate. Arsenic and tin will also be precipitated with antimony if they are present in the original precipitate. Should a separation be necessary, the precipitate is dissolved with hot concentrated hydrochloric acid, with the addition of crystals of potassium chlorate, from time to time, until the sulphides dissolve. The solution is placed in a Marsh apparatus, pure zinc added and the evolved gases passed into a neutral solution of silver nitrate. The black precipitate of silver antimonide and metallic silver are filtered off, washed free of arsenous acid, and the antimonide dissolved in strong hydrochloric acid (silver remains insoluble). The orange-colored antimony sulphide may now be precipitated by diluting the solution with water and passing in H_2S gas to saturation.

Minerals which contain antimony, when heated alone or with 3 to 4 parts of fusion mixture (K_2CO_3 and Na_2CO_3), on charcoal, yield dense white fumes, a portion of the oxide remaining as a white incrustation on the charcoal. A drop of ammonium sulphide placed upon this sublimate gives a deep orange stain.

Hydrolysis. Most of the inorganic antimony salts are decomposed by water, forming insoluble basic salts, which in turn break down to the oxide of antimony and free acid. An excess of tartaric acid prevents this precipitation.

Traces of Antimony. Nascent hydrogen liberated by the action of zinc and hydrochloric or sulphuric acid reacts upon antimony compounds with the formation of stibine. This gas produces a black stain on mercuric chloride or silver nitrate paper. Details of the procedure are given under the quantitative method for determining minute amounts of antimony.

Distinction between Antimonous and Antimonic Salts.

Chromates form with antimonous salts green chromic salts and antimonic salts.

Potassium Iodide reduces antimonic salts, free iodine being liberated.

[1] Van Nostrand's Chem. Annual, Olsen, 3d Ed.
[2] Cir. 35, U. S. Bureau of Standards.

ESTIMATION

The determination of antimony is required in the evaluation of antimony ores—stibnite, Sb_2S_3; valentinite, Sb_2O_3, etc. It is generally required in the complete analysis of minerals of nickel, lead, copper, silver, in which antimony generally occurs as a sulphide. The determination is required in the analysis of Britannia metal, bearing and antifriction metals, type metal and hard lead; in the analysis of certain mordants, antimony salts, vulcanized rubber, etc. It is looked for as an undesirable impurity in certain food products.

Preparation and Solution of the Sample

In dissolving the substance containing antimony it must be remembered that metallic antimony is practically insoluble in cold dilute hydrochloric, nitric or sulphuric acid and the oxides, Sb_2O_3 or Sb_2O_5, are precipitated in strong nitric acid. The element, however, is readily soluble in hydrochloric acid containing an oxidizing agent, such as nitric acid, potassium chlorate, chlorine, bromine, etc. The oxides of antimony are soluble in hydrochloric acid and the caustic alkalies.

Solution of Sulphide Ores, Low-grade Oxides, etc.[1]

0.5 to 1 gram of the finely ground ore, placed in a Kjeldahl flask, is mixed with 5 to 7 grams of ammonium sulphate, 1 gram of potassium sulphate, and 10 cc. of strong sulphuric acid. About 0.5 gram of tartaric acid, or a piece of filter paper, is added to reduce arsenic and antimony and the mixture heated, gradually at first, and then with the full Bunsen flame. The heating is continued until the carbon is completely oxidized and most of the free acid driven off, leaving a clean fusion from which ammonium sulphate is volatilizing. The melt is now cooled over the bottom and sides of the flask by gently rotating during the cooling.

About 50 cc. of dilute hydrochloric acid (1 : 1) are added and the melt dissolved by warming gently. The contents of the Kjeldahl flask are transferred to an Erlenmeyer flask, the Kjeldahl being rinsed out with 25 cc. of strong hydrochloric acid. Arsenic sulphide may now be precipitated with H_2S from the strongly acid solution, whereas antimony, etc., remain in solution. The sulphide is filtered off through a double filter, that has been moistened with hydrochloric acid (2 : 1), a platinum cone supporting the filter to prevent its breaking. The flask is rinsed out with hydrochloric acid (2 : 1). The precipitate is washed at least six times with the acid. Antimony passes into the filtrate together with other elements of the ore.

The filtrate is diluted with double its volume of warm water and then is saturated with hydrogen sulphide. Antimony sulphide, together with other elements of the Hydrogen Sulphide Group, will precipitate. These are washed with hydrogen sulphide water. Antimony sulphide may now be dissolved by addition of sodium sulphide and caustic solution (separation from Cu, Pb, Cd, Bi, etc.) (5 to 10 cc. of a mix of 60 grams Na_2S with 40 grams of NaOH diluted to 1000 cc.).

[1] Method of A. H. Low modified.

The solution containing the antimony is treated with about 2 grams of potassium sulphate and 10 cc. of strong sulphuric acid and heated as before, to destroy liberated sulphur and expel most of the free acid. The melt is dissolved in hydrochloric acid, and the antimony titrated according to one of the volumetric procedures given under "Volumetric Methods."

NOTE. An insoluble residue remaining from the acid extraction of the first melt may be dissolved by fusion with sodium hydroxide and extraction of the melt with hot water. If a precipitate forms when this alkaline solution is acidified with hydrochloric acid, the presence of barium sulphate is indicated.

Decomposition of the Ores by Fusion with Sodium Hydroxide.

Oxides. 0.5 to 1 gram of the powdered ore is mixed with about 10 grams of sodium hydroxide and placed in a thin-walled iron crucible of 60 cc. capacity. It is advisable to fuse a portion of the alkali hydroxide in the crucible with a pinch of potassium nitrate and then add the ore mixed with the remainder of the sodium hydroxide. The covered crucible is heated until the fusion becomes homogeneous. The melt is poured out on a large nickel crucible cover or shallow dish. On cooling, the cake is detached and placed in a casserole containing water, any adhering cake on the cover, or melt remaining in the iron crucible, being dissolved with dilute hydrochloric acid and added to the sample in the casserole. About 30 to 40 cc. of strong hydrochloric acid are now added and the mixture heated (casserole covered) until the melt has dissolved. Two to 3 grams of tartaric acid having been added to keep antimony dissolved, the solution is diluted to about 300 cc., and antimony is then precipitated as the sulphide with hydrogen sulphide. The treatment of the precipitate at this stage has been given in the "Solution of Sulphide Ores."

Sulphides. Howard and Harrison [1] recommend the following procedure for fusion of sulphide ores with caustic: 0.5 gram of the powdered ore is fused with a mixture of 8 grams of sodium carbonate and sodium peroxide, 1 : 1 in a nickel crucible. The cooled melt is dissolved with sufficient hydrochloric acid to neutralize the alkali and about 15 cc. of strong acid added in excess. The solution is diluted to 250 cc., antimony being kept in solution by addition of potassium chlorate. An aliquot portion of the solution is taken, antimony reduced by metabisulphite and titrated with iodine.

Treatment of Speisses, Slags, Mattes, etc.[2] 0.5 to 2 grams of the sample is treated with 10 to 15 cc. of strong nitric acid and the mixture taken to dryness. Fifteen cc. of strong hydrochloric acid are added and the sample transferred to a 350-cc. flask, additional hydrochloric acid being used to wash out the beaker. Arsenic is precipitated from the strong acid solution as the sulphide, and antimony determined in the filtrate.

Solution of Alloys. Alloys are generally decomposed by treatment with mixtures of hydrochloric acid together with an oxidizing agent—nitric acid, potassium chlorate, bromine, etc. The subject is taken up in detail in the chapter on alloys.

The alloy drillings are treated with strong hydrochloric acid, a little bromine added, and the mixture heated until the alloy dissolves, additional bromine being added from time to time if necessary. The excess bromine is removed by heating gently to boiling. The higher oxides are reduced by addition

[1] Phar. Jour., 1909, 83, 147.
[2] H. E. Hooper's method.

sodium metabisulphite and the sulphides precipitated, as usual, with hydrogen sulphide. Arsenic may now be volatilized by boiling, and antimony titrated with iodine or potassium bromate.

Alloys of Antimony, Lead and Tin. 0.5 to 1 gram of the finely divided alloy is warmed with 100 cc. of strong hydrochloric acid until the action subsides. Solid iodine is now added, in small quantities at a time, until the alloy completely dissolves. The excess of iodine is now removed by boiling and the small amount of free iodine remaining neutralized with a few drops of a weak solution of sodium thiosulphate. Although tin is oxidized to the higher state, antimony is not oxidized by iodine in acid solution beyond the trivalent form. The solution may now be titrated with standard iodine in presence of an excess of sodium bicarbonate according to the procedure given under the volumetric methods.

Hard Lead. The method of solution and titration are given under "Potassium Bromate Method for Determining Antimony."

Antimony in Rubber Goods.[1] Three grams of the finely rasped rubber are treated in a Kjeldahl flask with 40 to 45 cc. of strong sulphuric acid. A small quantity of mercury or mercury salt is added, together with a small piece of paraffine wax. The mixture is heated until the rubber is dissolved and the black liquid begins to clear. Two to 4 grams of potassium sulphate are then added and the heating continued until a colorless or pale yellow liquid is obtained. After cooling, 1 to 2 grams of potassium metabisulphite are added and an excess of tartaric acid. The liquid is diluted sufficiently to prevent the charring of the tartaric acid and boiled until the odor of sulphurous acid has disappeared. A few cc. of dilute hydrochloric acid are added, the liquid diluted to 200 cc., filtered through a dry filter, and 195 cc. titrated either with iodine or with potassium bromate (the latter in acid solution), as described under the volumetric procedures.

SEPARATIONS

Separation of Antimony (together with Members of the Hydrogen Sulphide Group), from Iron, Chromium, Aluminum, Cobalt, Nickel, Manganese, Zinc, the Alkaline Earths, and Alkalies. The acid solution of the elements is saturated with hydrogen sulphide, the elements of the Hydrogen Sulphide Group are precipitated as sulphides, the other elements remaining in solution. Antimony sulphide may be precipitated from an hydrochloric acid solution containing 15 cc. of strong acid per 100 cc. of solution; lead and cadmium are incompletely precipitated.

Separation of Antimony (together with Arsenic and Tin), from Mercury, Copper, Bismuth, Cadmium and Lead. The sulphides of antimony, arsenic, and tin are soluble in a mixture of sodium hydroxide and sodium sulphide, the soluble sulpho salts being formed, mercury, copper, bismuth, cadmium, and lead remaining as insoluble sulphides. The following procedure may be used for alloys free from members of other groups. The acid solution is treated with 3 to 5 grams of tartaric acid and diluted slightly (more tartaric acid being added if the solution becomes turbid), then poured into 300 cc. of a mixture of sodium sulphide and sodium hydroxide (150 cc. of the mix described under

[1] W. Schmitz, Chem. Zentralbl., 1911, ii, 1710. Analyst, 1912, p. 64.

"Solution of Sulphide Ores" diluted to 300 cc.). The mixture is warmed and the insoluble sulphides allowed to settle out. The solution is filtered free of the precipitate and the latter washed. The filtrate is acidified with hydrochloric or sulphuric acid and saturated with hydrogen sulphide. The sulphides of arsenic, antimony and tin are now filtered off and treated as described later.

Separation of Arsenic, Antimony, and Tin. The sulphides may be dissolved in concentrated hydrochloric acid by addition of potassium chlorate to oxidize the sulphur to sulphuric acid. This oxidation may be effected in the alkaline solution of the sulpho salts by addition of 30% hydrogen peroxide in small portions until the yellow solution is completely decolorized and then 1 to 2 cc. in excess, the solution then boiled to completely oxidize the sulphides to sulphates and to remove the excess of peroxide. The solution is then acidified, the precipitation of the sulphides and the subsequent filtration and resolution being avoided.

Removal of Arsenic. This may be accomplished by volatilizing arsenic as arsenic trichloride in a strong hydrochloric solution by boiling. If arsenic is to be determined the procedure given under the chapter on arsenic is followed, the arsenic being distilled in a current of hydrochloric acid gas. If arsenic is not desired it may be expelled by reducing the solution with sodium metabisulphite or potassium iodide and boiling. Antimony and tin remain in the concentrated acid solution.

The separation of arsenic from antimony and tin may be effected by removal of the former in a strong hydrochloric acid solution as described under the section "Preparation and Solution of the Sample," arsenic being precipitated by hydrogen sulphide, whereas antimony and tin remain in solution.

Separation of Antimony from Tin. Upon the removal of arsenic, antimony may be determined directly in the presence of tin by one of the volumetric methods given later. If a gravimetric separation is desired, it may be made according to Clark's method (C. N., Vol. 21, p. 124), which depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid, by hydrogen sulphide, whereas tin is not. The tin must be in the stannic form, otherwise the insoluble crystalline stannous oxalate will form.

If the mixture is acid, it is neutralized with caustic and twenty times the weight of the Sn and Sb present added in excess, e.g., 2 grams potassium hydroxide in excess for every 0.1 gram of tin and antimony present in the solution. About ten times as much of tartaric acid is now added as the maximum weight of the two metals, followed by 30% hydrogen peroxide to oxidize the tin. The excess of peroxide is removed by boiling. To the slightly cooled solution a hot solution of pure oxalic acid is added, 5 grams of oxalic acid for each 0.1 gram of the mixed elements. CO_2+O_2 are evolved. The solution is boiled for about ten minutes and the volume made up to about 100 cc. Hydrogen sulphide is rapidly passed into the boiling solution until a change from a white turbidity to an orange color takes place and antimony begins to precipitate. The passage of the gas is continued for fifteen minutes, the solution diluted with hot water to a volume of 250 cc. and hydrogen sulphide passed into the boiling solution for another fifteen minutes. The flame is now removed and the H_2S "gassing" continued for ten minutes longer. The precipitated antimony pentasulphide is filtered off in a weighed Gooch crucible.

It may be determined gravimetrically as Sb_2S_3, according to the procedure given later, by washing with 1% oxalic acid and dilute acetic acid, by decantation, the solutions being hot and saturated with hydrogen sulphide. The precipitate washed into the crucible is dried in a current of CO_2 at a heat of 280 to 300° and weighed as Sb_2S_3.

Tin may be determined electrolytically in the filtrate evaporated to about 150 cc., the oxalic acid being nearly neutralized with ammonia. See Electrolytic Determination of Tin.

Antimony may be separated from tin in a hot hydrochloric acid solution by addition of pure iron. The iron and tin sulphides are dissolved in concentrated hydrochloric acid plus a few crystals of potassium chlorate. The solution should contain about 10% hydrochloric acid, more hydrochloric acid being added as the iron dissolves. Antimony is precipitated as a metal.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ANTIMONY

The accuracy and rapidity of volumetric methods for the determination of antimony leave little to be desired in the estimation of this element, so that the more tedious gravimetric methods are less frequently used. The following procedures are given in view of possible utility in certain analyses.

Determination of Antimony as the Trisulphide, Sb_2S_3 [1]

Although hydrogen sulphide passed into a cold solution tends to precipitate Sb_2S_5, in hot strongly acid solutions, the lower sulphide, Sb_2S_3, tends to form. The higher sulphide is decomposed at 230° C. with formation of Sb_2S_3 and the volatilization of sulphur. A temperature[2] of 280 to 300° is even more favorable for this transformation. The method takes advantage of these conditions for formation of antimony trisulphide, in which form it is weighed.

Procedure. The solution of antimony, free from arsenic, is treated in an Erlenmeyer flask with strong hydrochloric acid until the solution contains about 20% of the concentrated acid. The mixture is heated to boiling and a slow current of hydrogen sulphide is passed into the hot solution until the precipitate passes from a yellow color through an orange and finally becomes a dark red to black color. The flask is agitated gently to coagulate the precipitate, which settles in a crystalline form. The solution is diluted with an equal volume of water, washing down the walls of the flask. A slight turbidity is generally seen, due to precipitation of a small amount of antimony that remains in solution in a strong acid solution. H_2S is now passed into the diluted solution until it becomes clear, thirty-five to forty minutes are usually sufficient to precipitate all of the antimony. The precipitate is transferred to a weighed Gooch crucible, washed with small portions of water containing hydrogen sulphide, and finally with pure water.

It is a common practice, at this juncture, to wash the precipitate with carbon disulphide or carbon tetrachloride to remove precipitated sulphur. Alcohol is now used, followed by ether, and the precipitate sucked dry.

[1] Method of Vortmann and Metzel modified.
[2] Paul, Z. anal. Chem. 31, 540 (1892).

The Gooch crucible is placed in a large combustion tube and heated in a current of dry, pure CO_2 at 130° C. for an hour. The temperature is now raised to 280 to 300° C. and the heating continued for two hours. The residue will consist of pure Sb_2S_3.

$$Sb_2S_3 \times 0.7142 = Sb, \text{ or } Sb_2S_3 \times 0.8568 = Sb_2O_3.$$

NOTES. Antimony may be determined by oxidation of the sulphide precipitate by means of fuming nitric acid. The mixture evaporated to dryness is ignited and the residue weighed as Sb_2O_4. The temperature of the ignition should be between 750 to 800° C. The volatile trioxide forms at a little above 950°. The procedure requires greater care than the sulphide method and possesses no advantages.

Pure carbon dioxide may be obtained from limestone placed in a Kipp generator. The gas is dried by passing it through strong sulphuric acid. It should be free from oxygen of the air. It is advisable to sweep out the air from the generator before attaching it to the combustion train. The air in the tube is swept out with carbon dioxide before heating the sample.

Property of Sb_2S_3, *m.w.*, 336.61; *sp.gr.*, 4.65; fusible and volatile; solubility, 0.000175 gram per 100 cc. H_2O; decomposed by hot H_2O; soluble in alkalies, NH_4HS, K_2S, conc. HCl.

Electrolytic Determination of Antimony [1]

The chief condition for the success of the electrolytic deposition of antimony in metallic form is the absence of polysulphides, since these substances prevent the element from being deposited, $2Sb + 3Na_2S_2 = 2Na_3SbS_3$. The formation of polysulphides may be prevented during electrolysis by addition of potassium cyanide to the solution,[2] $Na_2S_2 + KCN = Na_2S + KCNS$.

The results of this method, according to F. Henz,[3] are invariably 1.5 to 2% too high of the total antimony present in the solution. Treadwell and Hall recommend subtraction of a constant factor of 1.6% of the weight of the antimony deposited. The sample for analysis should contain not over 0.2 gram antimony.

Procedure. Antimony precipitated as the sulphide is washed and then dissolved off the filter by pouring pure sodium sulphide solution (sp.gr. 1.14) over the precipitate, the solution being caught in a weighed platinum dish, with unpolished inner surface. The total volume of the solution should be not over 80 cc. (if less than this, additional Na_2S solution is added to make up to 80 cc.). Sixty cc. of water followed by 2 to 3 grams of potassium cyanide (C.P.) are added and the cyanide dissolved by stirring with the rotating anode. The solution heated to 60 to 70° is electrolyzed with a current of 1 to 1.5 amperes, E.M.F. = 2 to 3 volts. Two hours are generally sufficient to deposit all the antimony. The light-gray deposit adheres firmly upon the cathode. Without breaking the current the solution is siphoned off, while fresh water is being added, until the current ceases to flow through the liquid. The cathode is washed thoroughly with water, followed by alcohol and ether and then dried at about 80°, cooled in a desiccator and weighed.

The antimony deposits may be removed by heating with a solution of alkali

[1] Method first proposed by Parrodi and Mascazzini, Z. anal. Chem., **18**, 587 (1879), modified by Luckow, Z. anal. Chem., **19**, 13 (1880), and later improved by Classen and Reiss, Berichte, **14**, 1629 (1881); **17**, 2474 (1884); **18**, 408 (1885); **27**, 2074 (1894). [2] Treadwell and Hall, Analytical Chemistry. [3] Z. anorg. Chem., **37**, 31 (1903).

polysulphide or by a mixture of equal parts of saturated solution of tartaric acid and nitric acid.

VOLUMETRIC METHODS

Potassium Bromate Method for Determining Antimony[1]

Outline. This method is of special value in determining antimony in hard lead and alloys. It was first suggested by Györy and later modified by Siedler, Nissensen and Rowell.[2] The process is based upon the oxidation of antimony from the trivalent to the pentavalent form by potassium bromate, the following reaction taking place:

$$KBrO_3 + 3SbCl_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O.$$

Standard Solutions.

Antimony Chloride Solution. Six grams of the C. P. pulverized metal are dissolved in 500 cc. of concentrated hydrochloric acid together with 100 cc. saturated bromine solution, more acid and bromine added if necessary to effect solution. After expelling the bromine by boiling, about 200 cc. concentrated hydrochloric acid are added and the whole made up to one liter. Fifty cc. =0.3 gram antimony.

N/10 Potassium Bromate Solution. 2.82 grams of C. P. salt are dissolved in water and made up to 1 liter. Theoretically 2.7852 grams are required, but the salt invariably contains potassium bromide as an impurity. The solution is standardized against 50 cc. of the antimony chloride solution, which has been reduced with sodium sulphite according to the standard scheme. One cc. of N/10 $KBrO_3$ = 0.006 gram Sb.

Antimony in Solder Metal and Alloys with Tin and Lead[3]

Procedure. Dissolve 2 grams of the sample of alloy in concentrated hydrochloric acid. When the metal is all in solution, add crystals of iodine until the solution is thoroughly permeated. The color at this point should be a deep purple. Boil until all of the iodine fumes have been driven out. The metallic antimony which did not go into solution in the hydrochloric acid should now be all dissolved. If it is not, add more iodine until the solution is complete. When all is in solution and the color has changed to a straw, cool, add a few cc. of starch solution. If a blue color appears, due to an excess of iodine, run in N/10 sodium thiosulphate solution until colorless. In case there is no blue color developed, add N/10 iodine until a faint blue appears. Now add 50 cc. of a saturated solution of Rochelle salts. Make alkaline to litmus by adding 25% sodium hydrate solution. Then make slightly acid with HCl and finally alkaline with sodium bicarbonate. Cool and titrate with N/10 iodine.

NOTE. "The method gives very good results. I have checked it up when there was one-tenth of a gram known antimony present and the results were within a reasonable limit of accuracy." [1]

[1] S. Györy, Zeit. Anal. Chem., 32, 415 (1893). J. B. Duncan, Chem. News, 95, 49 (1907).

[2] H. W. Rowell, Jour. Soc. Chem. Ind., XXV, 1181.

[3] Method communicated to author by Mr. B. S. Clark.

Methyl Orange. 0.1 gram M. O. per 100 cc. of distilled water. The indicator should be free from sediment.

Saturated Bromine Solution. 500 cc. concentrated hydrochloric acid saturated with 70 cc. of bromine.

Procedure. ***Solution.*** One gram of the finely divided alloy is brushed into a 500-cc. beaker, 100 cc. of concentrated hydrochloric acid and 20 cc. of saturated bromine solution are added. The beaker is covered and placed on the steam bath until the metal dissolves. It may be necessary to add more bromine and acid to effect complete solution. In case the oxides of antimony and tin separate out and do not redissolve, fusion with sodium hydroxide may be necessary. Bromine is now expelled by boiling the solution down to about 40 cc.

Reduction. One hundred cc. of concentrated hydrochloric acid and 10 cc. of a fresh saturated solution of Na_2SO_3 are added and the solution boiled down to 40 cc., on a sand bath, to expel arsenic and the excess of normal sodium sulphite. Samples high in arsenic may require a repetition of the reduction.

Titration. The cover and sides of the beaker are rinsed down with 20 cc. of hydrochloric acid (sp.gr. 1.2) followed by a few cc. of hot water and the solution heated to boiling on a sand bath. The standard bromate solution is now run into the hot solution of antimony to within 2 to 3 cc. of the end-point, this having been determined in a preliminary run with methyl orange added in the beginning, 4 drops of methyl orange are added and the titration completed cautiously until the color of the indicator is destroyed. If iron or copper is present the final product will appear yellow. Since the end-reaction is slow the last portion of the reagent should be added drop by drop with constant stirring.

1 cc. N/10 $KBrO_3$ = 0.006 gram Sb.

NOTES. Since antimony chloride begins to volatilize at 195° C. and boils at 220° C. it is advisable not to carry the concentration too far while expelling arsenic.

Lead, copper, zinc, tin, silver, chromium, and sulphuric acid have no effect upon the determination, but large quantities of calcium, magnesium, and ammonium salts tend to make the results high. Low[1] found that copper produced high results, approximately .012% too high for every 0.1% of copper present. The author (W.W.S.) finds, however, that with the procedure given above, amounts of copper as high as 15% produced no difficulty beyond a yellow coloration of the solution. With larger amounts of copper, the end-point became difficult to detect owing to the depth of this yellow color, so that in case of brass and copper alloys, the method must be modified by a procedure for removal of the copper. Lead up to 95% caused no difficulty. Iron, in amounts such as are commonly met in alloys of lead, does not interfere.

During the course of analysis antimony may be isolated as the sulphide; this is dissolved in strong hydrochloric acid, and reduced and concentrated to expel arsenic that may be present as a contamination, and the resulting solution titrated with potassium bromate as directed above.

Sources of Error. (*a*) Imperfect volatilization of arsenic. (*b*) Incomplete expulsion of SO_2. (*c*) Over-titration if insufficient hydrochloric acid is present.

No loss of antimony occurs at temperatures below 120° C.

Potassium Iodide Method for Determining Antimony

Procedure. To 1 gram of fine sawings or filings in a 16-oz. Erlenmeyer flask add 60 cc. of concentrated hydrochloric acid and heat on an asbestos board or on the water bath just below boiling. When hydrogen is no longer evolved, decant

[1] A. H. Low, Technical Methods of Ore Analysis.

the liquor and wash twice with concentrated hydrochloric acid, retaining the antimony in the flask. Now dissolve the antimony by adding 15 cc. of concentrated hydrochloric acid and solid potassium chlorate, a few crystals at a time, until the antimony is in solution, the liquid being kept hot. Expel chlorine by boiling, add 50 cc. of concentrated hydrochloric acid and again bring to boiling. Cool and add 20 cc. of 20% potassium iodide solution and 1 cc. of carbon disulphide or tetrachloride. Titrate the liberated iodine with tenth-normal sodium thiosulphate. The brown color will gradually disappear from the solution and the last traces of free iodine will be collected in carbon disulphide or carbon tetrachloride, giving a pink color. When this pink color disappears the end-point has been reached.

One cc. N/10 $Na_2S_2O_3$ = .006 gram of Sb.

$Na_2S_2O_3$ is standardized against .3 gram antimony as in case of Potassium Bromate Method, the above procedure, however, being followed. Antimony must be free from copper and arsenic.

NOTES. The following reversible reaction is of interest: "R" representing a trivalent metal with oxidation to pentavalent form.

$$R_2O_3+2I_2+2H_2O=R_2O_5+4HI.$$

The reaction goes to the right when an alkali is present to neutralize the free acid formed; e.g., Mohr's process for determining arsenic by titration of the lower oxide with iodine in presence of sodium bicarbonate. The reaction goes to the left in presence of strong acid; e.g., Weller's process for the determination of antimony in an acid solution.

The solution should not contain more than $\frac{1}{8}$ of its volume of hydrochloric acid (sp.gr. 1.16), since too much hydrochloric acid gives high results, owing to the action of hydrochloric acid on potassium iodide. Too little acid leads to the separation of basic iodides and chlorides of antimony. The solution is best boiled down to 20% hydrochloric acid (above strength).

Stannous chloride may be used in place of thio-sulphate in titration of iodine.

$$SbCl_5+2KI=SbCl_3+2KCl+I_2 \quad \text{and} \quad I_2+SnCl_2+2HCl=SnCl_4+2HI.$$

Determination of Antimony by Oxidation with Iodine

The procedure originated by Mohr and modified by Clark, depends upon the reaction $Sb_2O_3+2I_2+2H_2O=Sb_2O_5+4HI$.

The reaction takes place when iodine is added to a solution of antimonous salt in presence of an excess of alkali bicarbonate. In an acid solution oxidation with iodine does not go beyond Sb_2O_3.

Procedure. ***Solution.*** The sample is brought into solution by one of the procedures given under "Preparation and Solution of the Sample." Alloys of antimony, lead, and tin are treated according to directions given for this combination.

Titration. To the hydrochloric acid solution of antimony is added tartaric acid or Rochelle salts, the excess of the acid neutralized with sodium carbonate, the solution made barely acid with hydrochloric acid and a saturated solution of sodium bicarbonate added in the proportion of 10 cc. bicarbonate solution for each 0.1 gram of Sb_2O_3. Starch is added as an indicator and the solution titrated with N/10 iodine.

1 cc. N/10 iodine = 0.006 gram Sb.

NOTE. The titration should be made immediately upon addition of the sodium salts.

Other Procedures

Permanganate Method

Antimonous salts may be titrated with standard potassium permanganate. The iron value for the permanganate multiplied by 1.075 or the oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) value multiplied by 0.9532, will give the antimony value.[1]

Indirect Evolution Method

The method depends upon the evolution of H_2S from the sulphides of antimony decomposed by strong hydrochloric acid, the amount of hydrogen sulphide being the same for either Sb_2S_3 or Sb_2S_5, the following reactions taking place:

1. $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$.
2. $Sb_2S_5 + 6HCl = 2SbCl_3 + S_2 + 3H_2S$.

The details of the method are practically the same as determination of sulphur by the evolution method in the analysis of iron and steel. See Chapter on Sulphur. The antimony sulphide precipitate is placed in the evolution flask, strong hydrochloric acid added with an equal volume of water and the evolved hydrogen sulphide absorbed in an ammoniacal solution of cadmium chloride. The precipitated cadmium sulphide is then titrated with iodine in an acid solution.

One cc. N/10 I = 0.001604 gram S, since 3S = 2Sb, therefore Sb = S × 2.499, hence, 1 cc. N/10 I = 0.00401 gram Sb.

Preparation of Standard Iodine Solution. An approximate tenth normal solution is made by dissolving 12.7 grams of commercial iodine, roughly weighed on a watch-glass, in 200 cc. of water containing about 25 grams of potassium iodide, solution being effected in a graduated liter flask. After making up to 1000 cc. with distilled water, the reagent is transferred to a dark-colored bottle, to protect it from light. It is advisable to make up 5 to 10 liters at a time for laboratories where the solution is in constant demand. After standing several hours, the reagent is standardized by running a portion from a burette into 100 cc. of tenth normal arsenous acid (see page 204) until a faint yellow color is perceptible. In presence of starch indicator a faint blue color is obtained.

100 divided by the cc. of iodine required gives the factor for a N/10 solution.

Example. If 98.5 cc. of iodine are required, 100 ÷ 98.5 = 1.0152 N/10 or .10152 normal.

Tenth normal arsenous acid solution contains 4.953 grams of As_2O_3, per liter, dissolved in sodium hydroxide and made up according to directions given on page 204. The oxide is seldom pure, so that allowance must be made for impurities. For example, the acid containing 99.56 per cent As_2O_3 would require 4.953 ÷ .9956 = 4.97 grams per liter of solution.

Commercial iodine may contain chlorine, bromine, cyanogen and water. It may be purified by repeated sublimation ("Analytical Chemistry," Treadwell and Hall, IV Ed., page 646, or "A Treatise on Quantitative Inorganic Analysis" (1913), by J. W. Mellor, page 288). There is no advantage in taking the theoretical amount of purified iodine, however, since the reagent changes in strength on standing.

Potassium iodide augments solution of iodine, which is sparingly soluble in water.

The iodine may be standardized by titrating a definite volume with N/10 sodium thiosulphate. See page 204.

[1] Technical Methods of Ore Analysis, by A. H. Low.

Determination of Small Amounts of Antimony[1]

The determination depends upon the fact that when antimony compounds are acted upon in acid solution by nascent hydrogen the gas stibine is evolved, which forms a black compound with silver nitrate. The method is very similar to Allen and Palmer's modification of the Gutzeit procedure for arsenic, differing, however, in the facts that heating is necessary to evolve completely the stibine, the presence of iron is not required, and stannous chloride is not used.

Procedure. The material is brought into solution with water, or by treatment with hydrochloric acid, or hydrochloric acid and an oxidizing agent ($KClO_3$ or Br) with subsequent evaporation to dryness on the steam plate or water bath, or by fusion with sodium carbonate followed by acid extraction. If arsenic is present, the solution, contained in a distillation flask, is reduced with ferrous sulphate or chloride and arsenic distilled off in a current of HCl gas, according to the procedure outlined under Arsenic. The volume of the solution is reduced from about 200 cc. to 50–60 cc.[2] Antimony is now isolated by continuing the distillation with addition of zinc chloride to raise the boiling-point of the solution. Thirty cc. of a saturated solution of zinc chloride are added to the liquor in the flask and antimony distilled, hydrochloric acid (sp.gr. 1.2) being added through a separatory funnel, drop by drop, to replace the solution evaporated. The first fifty cc. of the distillate will contain all the antimony, present in small amount. The excess of acid is carefully neutralized with sodium carbonate, leaving the solution slightly acid. The mixture is placed in the modified Gutzeit apparatus, pure zinc shot added, and the apparatus connected up as described for determining traces of arsenic, Fig. 2. In place of the mercuric chloride, silver nitrate paper is used for obtaining the stain, as this reagent is more sensitive to stibine. The apparatus is placed in warm water (about 60° C.) for two hours. The silver nitrate paper is then removed, immersed in 10% solution of sodium thiosulphate to fix the stain and washed with distilled water to remove the silver nitrate. The paper is then dried and compared with a standard set of stains made by placing known amounts of antimony in solutions of like material examined, and proceeding according to the outline given.

Notes. Potassium antimonyl tartrate may be taken for the standard antimony solution. 0.2765 gram of the salt is diluted to a liter and 10 cc. of this stock solution is diluted to 1 liter. 10 cc. of this final solution is equivalent to 0.01 milligram of antimony. Stains representing 0.005 to 0.05 milligram antimony are suited for the test.

Silver nitrate paper. This is made by dipping sheets of filter paper in a 0.4% solution of silver nitrate, running through the mangle to remove the excess of silver nitrate, drying and cutting into strips according to the procedure recommended for the paper used in the Gutzeit method for arsenic.

Blank runs should be made with the reagents and the blanks deducted from the stains obtained in the regular tests. If possible, arsenic and antimony-free reagents should be used.

The author is indebted to Mr. J. P. Kelly for his review and criticism of this chapter.

[1] Method suggested by C. R. Sanger, communicated to the author by Mr. J. P. Kelly.

[2] During the removal of arsenic the temperature of the solution should not rise above 125° C., since a loss of antimony occurs above this point. It is advisable, therefore, to place a thermometer in the flask, and observe the temperature during the distillation.

ARSENIC

WILFRED W. SCOTT

As_4 *at.wt.* 74.96— *cryst.* *sp.gr.* 5.73 *m.p.* 850 *b.p.* *subl.* 554°
$<$ 360°
amorp. **4.72** **....**

Oxides, **As_2O_3, As_2O_5.**[1]

DETECTION

Hydrogen sulphide precipitates the yellow sulphide of arsenic, As_2S_3, when passed into its solution made strongly acid with hydrochloric acid. If the solution contains more than 25% hydrochloric acid, (sp.gr. 1.126) the other members of the hydrogen sulphide group do not interfere, as they are not precipitated from strong acid solutions by hydrogen sulphide. Arsenic sulphide is soluble in alkaline carbonates. (Antimony sulphide, Sb_2S_3, reddish yellow, is insoluble in alkaline carbonates.)

Volatility of the chloride, $AsCl_3$, is a means of separation and distinction of arsenic. Details of the procedure are given under "Separations." The distillate may be tested for arsenic as directed above.

Traces of arsenic may be detected by either the Gutzeit or Marsh test for arsenic. Directions for the Gutzeit test are given at the close of the volumetric procedures.

Distinction between Arsenates and Arsenites. Magnesia mixture precipitates white, $MgNH_4AsO_4$, when added to ammoniacal solutions containing arsenates, but it produces no precipitate with arsenites.

Red silver arsenate and yellow silver arsenite are precipitated from neutral solutions by ammoniacal silver nitrate. An arsenate gives a yellow precipitate with ammonium molybdate solution.

ESTIMATION

The determination of arsenic is required in the valuation of native arsenic, white arsenic, As_2O_3; ores of arsenic—orpiment, As_2S_3; realgar, As_2S_2; pyrargyrite, As_3Sb_3; arsenopyrite, or mispickel, FeSAs; cobaltite or cobalt glance, CoSAs; smaltite, $CoAs_2$; niccolite, NiAs. The substance is estimated in copper ores, in speiss, regulus; in iron precipitates (basic arsenate). It is determined in paint pigments, Scheel's green, etc. The element is determined in shot alloy and in many metals. It is estimated in germicides, disinfectants, and insecticides—Paris green, lead arsenate, zinc arsenite. Traces are looked for in food products and in substances where its presence is not desired.

Preparation and Solution of the Sample

In dissolving arsenic compounds it will be recalled that the oxide, As_2O_3, is not readily acted upon by dilute acids—hydrochloric or sulphuric. The compound is soluble, however, in alkaline hydroxides and carbonates. Nitric

[1] Van Nostrand's Chem. Annual—Olsen—3d Ed.

acid oxidizes As_2O_3 to the higher oxide, As_2O_5, which is soluble in water. The sulphides As_2S_3 and As_2S_5 are practically insoluble in hydrochloric or sulphuric acids, but are dissolved by the fixed alkalies and alkali sulphides. All arsenites, with the exception of the alkali arsenites, require acids to effect solution.

Pyrites Ore and Arseno-pyrites. The amount of the sample may vary from 1 to 20 grams,[1] according to the arsenic content. The finely ground sample in a large casserole is oxidized by adding 10 to 50 cc. of bromine solution (75 cc. KBr+50 cc. liquid Br+450 cc. H_2O) covering and allowing to stand for fifteen minutes, then 20 to 50 cc. of strong nitric acid are added in three or four portions, allowing the action to subside upon each addition. The glass cover is raised by means of riders, and the sample evaporated to dryness on the steam bath; 10 to 25 cc. of hydrochloric acid are now added and the sample again taken to dryness. Again 10 to 25 cc. of hydrochloric acid are added and the sample taken to dryness. Finally 25 cc. of hydrochloric acid and 75 cc. of water are added, and the mixture digested over a low flame until all the gangue, except the silica, is dissolved. The solution is now examined for arsenic by distillation of the arsenic after reduction, the distillate being titrated with standard iodine solution according to directions given later.

Arsenous Oxide. The sample may be dissolved in caustic soda, the solution neutralized with hydrochloric acid, and the resulting sample titrated with iodine according to the regular procedure.

Arsenic Acid, Alkali Arsenates, etc. The sample is dissolved in 20 to 25 cc. of dilute sulphuric acid, 1 : 1, in an Erlenmeyer flask, and reduced by addition of 3 to 5 grams of potassium iodide, the action being hastened by placing the mixture on a steam bath. The iodine liberated is exactly neutralized with thiosulphate and the arsenous acid titrated with iodine according to the procedure given later. If a N/10 iodine solution is to be used, the sample should not contain over .37 gram arsenic. A 10-gram sample may be taken, made up to a definite volume and aliquot parts taken for analysis.

Arsenic in Sulphuric Acid. ***Arsenous acid*** may be titrated directly with iodine in a 20- to 50-gram sample, which has been diluted to 200 to 300 cc. with water and nearly neutralized with ammonium hydroxide and then an excess of sodium acid carbonate added, followed by the iodine titration.

Arsenic Acid in Sulphuric Acid. Twenty-five cc. of the acid containing about 0.1% arsenic or a larger volume in case the percentage of arsenic is less than 0.1% As_2O_3 (the sp.gr. of the acid being known) are measured out into a short-necked Kjeldahl flask. About half a gram of tartaric acid and 2 grams of fused, arsenic-free potassium bisulphate are added and the acid heated over a low flame until the liberated carbon is completely oxidized and the acid again becomes clear, e.g., a pale straw color. It is not advisable to heat to violent fuming, as a loss of arsenic is then apt to occur. The cooled acid is poured into about 300 cc. of water, the excess acid nearly neutralized with ammonia, bicarbonate of soda added in excess and the arsenous acid titrated with standard iodine. Total arsenic as As_2O_3 minus arsenous arsenic as As_2O_3 = arsenic arsenic in terms of As_2O_3. This result multiplied by 1.1616 = As_2O_5.

Arsenic in Hydrochloric Acid. The arsenic in 20 to 100 cc. sample is reduced by ferrous chloride, the arsenic distilled according to directions given later, and the distillate titrated with iodine.

[1] 0.1% arsenic determined on a 20-gram sample.

Arsenic in Organic Matter.[1] 0.2 to 0.5 gram of the sample finely powdered is oxidized by mixing with 10 to 15 grams of sodium carbonate and sodium peroxide, 1 : 1, in a nickel crucible, a portion of the fusion mixture being spread over the charge. After heating gently for fifteen minutes, the fusion is completed by heating to dull redness for five minutes longer. The contents of the crucible are rinsed into an Erlenmeyer flask after extraction with water, and the solution made acid with dilute sulphuric acid, 1 : 1. The mixture is boiled down to 100 cc., 1 to 2 grams of potassium iodide added and the solution further concentrated to about 40 cc. Iodine is reduced with sulphurous acid or thiosulphate, the solution diluted with hot water and saturated with hydrogen sulphide. Arsenous sulphide is filtered off, washed, dissolved in 15 to 20 cc. of half-normal sodium hydroxide and 30 cc. of hydrogen peroxide (30%) solution added, and the solution boiled. About 12 cc. of dilute sulphuric acid, 1 : 1, are added, together with 1 to 2 grams of potassium iodide, the solution concentrated to 40 cc. and free iodione reduced with thiosulphate as before. Arsenic is now titrated, with standard iodine, upon neutralization of the free acid with sodium hydroxide and sodium acid carbonate.

Lead Arsenate. Ten grams of the thoroughly mixed paste or 5 grams of the powder are dissolved by treating with 25 cc. of 10% hot sodium hydroxide solution, and diluted to 250 cc. An aliquot part, 50 cc. (=2 grams paste and 1 gram powder) is placed in an Erlenmeyer flask and 20 cc. of dilute sulphuric acid, 1 : 1, added, and the solution diluted to 150 cc. About 3 grams of solid potassium iodide are added and the solution boiled down to about 50 cc. (but not to fumes). The liquor will be colored yellow by free iodine. Tenth normal sodium thiosulphate is added drop by drop until the free iodine is neutralized (solution loses its yellow color), it is now diluted to about 250 cc. and the free acid neutralized by ammonium hydroxide (methyl orange indicator), then made slightly acid with dilute sulphuric acid, and an excess of bicarbonate of soda added. The arsenic is titrated with standard iodine.

The arsenic may be reduced by placing the 50-cc. sample in a Kjeldahl flask, adding 25 cc. of strong sulphuric acid (1.84 sp.gr.), ½ gram tartaric acid and 2 grams acid potassium sulphate, $KHSO_4$, and digesting over a strong flame until the organic matter is destroyed and the solution is a pale yellow color. The cooled acid is diluted and neutralized, etc., as directed above.

Water-soluble Arsenic in Insecticides. Rapid Works Test. Two grams of the paste is digested with 1000 cc. of water at 90° C. for five minutes, in a graduated 1000-cc. flask. An aliquot portion is filtered and the arsenic determined by the Gutzeit method.

Water-soluble arsenite may be titrated directly with iodine in presence of sodium bicarbonate.

Zinc Arsenite. About 5 grams of powder or 10 grams of paste are taken and dissolved in a warm solution containing 300 cc. of water and 25 cc. of strong hydrochloric acid. The cooled solution is diluted to 500 cc. and 100-cc. portions taken for analysis. The acid is partly neutralized with ammonium hydroxide and 50 cc. of a saturated solution of ammonium oxalate added (to prevent precipitation of the zinc as $ZnCO_3$), and an excess of sodium bicarbonate, $NaHCO_3$. Arsenic is now titrated with iodine as directed later.

Soluble Arsenic in Zinc Arsenite. One gram sample is rubbed into an

[1] Little, Cahan, and Morgan, Jour. Chem. Soc., 95, 1477 (1909).

emulsion with several portions of water until the whole is in suspension. The cloudy liquor is diluted to 1000 cc. and a portion filtered through a ¼-in. asbestos mat on a perforated plate, the asbestos being covered with a layer of filter paper. The first 50 cc. are rejected. One hundred cc. of the clear filtrate (= 0.1 gram) is treated with 10 cc. of strong sulphuric acid, 0.05 gram, Fe_2O_3 (use ferric ammonium sulphate) and ½ cc. of 80% stannous chloride solution and heated until colorless. Arsenic is now determined by the Gutzeit method, using the larger-sized apparatus.

Arsenic in Mispickel. One gram of the finely powdered mineral is fused in a nickel crucible with about 10 grams of a mixture of potassium carbonate and nitric acid, 1 : 1,[1] and the melt extracted with hot water. Two hundred cc. of a saturated solution of SO_2 is added to the filtrate to reduce the arsenic, the excess of SO_2 then expelled by boiling, the solution diluted with dilute sulphuric acid, and arsenic determined in the filtrate.

Arsenic in Steel, Iron, Pig Iron, etc. One to 50 grams of steel, etc., may be treated according to the scheme for pyrites. If a large sample is taken, it is advisable to treat it in a 500-cc. flask, connected with a second flask containing bromine, to guard against loss of arsenic by volatilization. When the sample has dissolved it is taken to dryness (the bromine in the second flask being combined with it) and treated as directed in pyrites. Arsenic chloride, $AsCl_3$, is transferred to the distilling flask with strong hydrochloric acid, and arsenic separated from the iron by volatilization of reduced chloride according to the procedure given below.

Arsenic in Copper. Arsenic is precipitated with iron by the basic acetate method, and thus freed from copper. Details of procedure are given under the determination of impurities in copper in the chapter on the subject.

SEPARATIONS

Isolation of Arsenic by Distillation as Arsenous Chloride [2]

By this method arsenic may be separated from antimony, tin, and from other heavy metals. It is of special value in the direct determination of arsenic in iron ores, copper ores, and like products and has a wide application. The procedure depends upon the volatility of arsenous chloride at temperatures lower than the other heavy metals. In a current of HCl gas, arsenous chloride begins to volatilize below 108° C., and is actively volatile at 120° C.; antimony starts to volatilize at 125° C., but is not actively volatile until a temperature of 180° has been reached. The boiling-point of arsenous chloride, $AsCl_3$, is 130.2°; antimony trichloride, $SbCl_3$, is 223.5°; and that of stannous chloride, $SnCl_2$, is over 603°; other chlorides having still higher boiling-points. Tin in its higher form, $SnCl_4$, is readily volatile, boiling-point is 114° C., so that it is necessary to have it in its divalent form to effect a separation from arsenic. When heavy metals are present in the residue remaining from the arsenic distillate, or when zinc chloride is added to raise the boiling-point, antimony

[1] The ore may be brought into solution by fusion with a mixture of sodium carbonate, potassium nitrate and zinc oxide, 1 : 1 : 2. The fusion being made in a platinum dish. The potassium iodide procedure may be followed for reduction of arsenic. (See Lead Arsenate.)

[2] J. E. Stead's Method. R. C. Roark and C. C. McDonnell, Jour. Ind. Eng. Chem., VIII, 4, 327 (1916).

may also be separated by distillation by carrying the solution to near dryness, adding concentrated HCl by means of a separatory funnel, drop by drop, during further distillation of the concentrate. Arsenic may be determined in the distillate (first portions) either gravimetrically or volumetrically.

Procedure. If arsenic is present as arsenic chloride, as prepared in the method for solution of iron ores, the sample may be transferred directly to the distillation flask by means of concentrated, arsenic-free hydrochloric acid. If a preliminary separation of other metals has been made and arsenic is present (along with antimony and tin) as a sulphide, it is oxidized by addition of concentrated HCl and sufficient potassium chlorate to cause solution and oxidation of free sulphur, and the chlorate decomposed by evaporation to

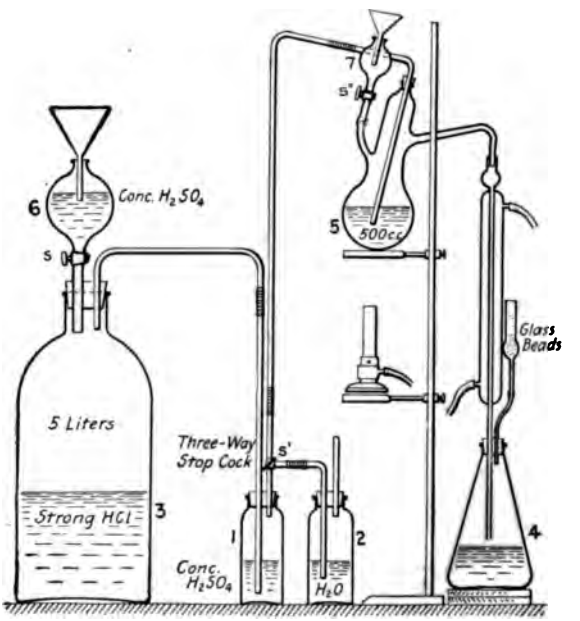


FIG. 1.—Apparatus for the Distillation of Arsenous Acid.

dryness; or if preferred, by evaporation of the alkaline solution to dryness, oxidation with fuming nitric and re-evaporation to dryness to expel the nitric acid. The residue is taken up with hydrochloric acid and washed into the flask with strong hydrochloric acid as directed above.

Distillation. The sample, in a half-liter distilling flask (Fig. 1, "5") is made up to about 150 cc. with concentrated hydrochloric acid and about 5 grams of cuprous chloride, Cu_2Cl_2, are added. The apparatus is connected up as shown in the illustration, Fig. 1. The end of the condenser dips into 400 cc. of cold water in a large beaker (1 liter) or flask ("4"). The solution is cooled by placing it in ice-water or cold running water. The sample is saturated with dry hydrogen chloride gas generated by dropping concentrated sulphuric acid into strong hydrochloric acid ("3") and passing the gas through

sulphuric acid ("1") (sp.gr. 1.84) as shown in cut. When the point of saturation is reached the gas begins to bubble through the solution instead of being absorbed by it. When this occurs, heat is applied and the solution brought to boiling, the current of HCl gas being continued. At a temperature of 108 to 110° C. the first 100 cc. will contain practically all of the arsenic. About two-thirds of the solution is distilled off. It is advisable to add more hydrochloric acid to the residue in the flask, together with cuprous chloride, and repeat the distillation into a fresh lot of water. This may be done during the estimation of arsenic in the first distillate.

Arsenic may be determined in the distillates either gravimetrically or volumetrically. The volumetric procedures for arsenic, in this isolated form, are generally to be preferred, since they are both rapid and accurate. For amounts over 0.5% arsenic, the iodine method is recommended, for smaller amounts (arsenic in crude copper), precipitation with silver nitrate and titration of the silver salt is best. Exceedingly small amounts are best determined by the Gutzeit method, page 40.

Commercial hydrochloric acid invariably contains arsenic, so this must be purified by redistillation in presence of an oxidizing agent to oxidize the arsenic to the non-volatile arsenic pentachloride, $AsCl_5$, form, (Fig. 5) or by treatment with H_2S and filtration. A blank run should be made on the reagents used, especially when traces of arsenic are to be determined.

Separation of Arsenic from Antimony and Tin by Precipitation as Sulphide in a Strong Hydrochloric Acid Solution

This procedure, recommended by Neher,[1] depends upon the insolubility of the sulphide of arsenic in strong hydrochloric acid, whereas that of antimony dissolves. The sulphide of tin is also soluble.

Procedure. The metals present in their lower conditions of oxidation are precipitated as sulphides in presence of dilute hydrochloric acid (5% solution) to free them from subsequent groups (Fe, Al, Ca, etc.). The soluble members of the Hydrogen Sulphide Group are now dissolved and separated from copper, lead, etc., by caustic as follows: The greater part of the washed precipitate is transferred to a small casserole, that remaining on the filter paper is dissolved off by adding to it a little hot dilute potash solution, catching the filtrate in the casserole. About 5 grams weight of solid potassium hydroxide or sodium hydroxide is added to the precipitate. Arsenic, antimony, and tin sulphides dissolve. The solution is filtered if a residue remains, and the filter washed. This preliminary treatment is omitted if alkaline earths and alkalies are the only contaminating elements present.

The casserole, containing arsenic, antimony, and tin, is covered with a perforated clock-glass and chlorine conducted into it until all the alkali is decomposed (one-half to three-quarters hour); the higher state of oxidation results. The clock-glass is now removed and the solution evaporated to half volume. An equal volume of hydrochloric acid is added, and the solution again evaporated to decompose potassium chlorate. When free from chlorine, the acid solution is washed into an Erlenmeyer flask, cooled by ice to 0° C. and two volumes of

[1] Fred Neher, Z. Anal. Chem., 32, 45.

cooled, concentrated, hydrochloric acid added. H_2S gas is rapidly passed into this solution for an hour and a half. The flask is now stoppered and allowed to stand another hour or so. The yellow arsenic sulphide, As_2S_5, is filtered through a weighed Gooch crucible, washed with hydrochloric acid, 2 : 1, until free from antimony, i.e., the washing upon dilution remains clear. The residue is now washed with water, followed by alcohol, and may be dried and weighed as As_2S_5, or determined volumetrically. Antimony and tin are determined in the filtrate.

The sulphide may be dissolved in concentrated sulphuric acid by heating to sulphuric acid fumes and until the solution becomes clear. No arsenic is lost, provided the heating is not unduly prolonged. Fifteen to twenty-five minutes is generally sufficient to dissolve the sulphide and expel SO_3, etc. The acid may be neutralized with ammonia or caustic, made again barely acid and then alkaline with bicarbonate of soda, and arsenous acid titrated with iodine.[1]

GRAVIMETRIC METHODS FOR DETERMINATION OF ARSENIC

As in the case of antimony, the accuracy and rapidity of the volumetric methods for the determination of arsenic make these generally preferable to the more tedious gravimetric methods. The following methods, however, are of value in certain analytical procedures.

Determination of Arsenic as the Trisulphide, As_2S_3

Arsenic acid and arsenates should be reduced to the arsenous form before precipitation as the sulphide. The procedure is especially adapted to the isolation of arsenic from other elements, when this substance is present in the solution in appreciable quantities, advantage being taken of the extreme difficulty with which arsenous sulphide, As_2S_3, dissolves in hydrochloric acid solution.

Procedure. The solution containing arsenic in the arsenious form is made strongly acid with hydrochloric acid and hydrogen sulphide passed into the cold solution to complete saturation. The hydrogen sulphide pressure generator is recommended for this treatment. Figs. 3 and 4. The precipitate is filtered into a weighed Gooch crucible (previously dried at 105° C.), the compound dried at 105° C. to constant weight and weighed as As_2S_3.

Factors. $As_2S_3 \times 0.6091 =$ grams As.
$As_2S_3 \times 0.8042 =$ grams As_2O_3.
$As_2O_3 \times 1.1616 =$ grams As_2O_5.
$As_2O_5 \times 1.3134 =$ grams $H_3AsO_4 \cdot \frac{1}{2}H_2O$.
$As_2S_3 \times 1.2606 =$ grams As_2S_5.

NOTE. Arsenic may also be determined as arsenic sulphide by passing a rapid stream of H_2S into a cooled solution of arsenic acid containing at least two parts of concentrated hydrochloric acid for each part of water present in the solution.

[1] J. and H. S. Pattinson, Jour. Soc. Chem. Ind., 1898, p. 211.

Determination of Arsenic as Magnesium Pyroarsenate

The method worked out by Levol depends upon the precipitation of arsenic as $MgNH_4AsO_4 \cdot 6H_2O$, when magnesia mixture is added to an ammoniacal solution of the arsenate. Although 600 parts of water dissolve 1 part of the salt, it is practically insoluble in a 2½ per cent ammonia solution, 1 part of the anhydrous salt requiring 24,558 parts of the ammonia water according to Virgili.[1] The compound loses 5½ molecules of water at 102° C. and all of the water when

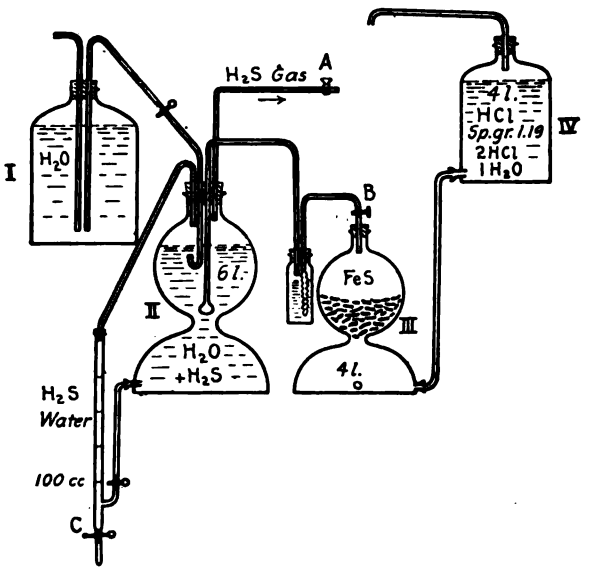


FIG. 2.—Urbasch's Hydrogen Sulphide Generator.

The apparatus designed by Urbasch (Chem. Zeit. (1910) **34**, 1040. The Analyst (1910) **35**, 558), shown in Fig. 2, enables a constant supply of gas and its saturated aqueous solution to be obtained. The bottle IV is charged with hydrochloric acid, and iron sulphide is placed in III. The hydrogen sulphide is passed through the water in II until a saturated solution is obtained. Water is placed in I and II. If gas is required the taps *A* and *B* are opened and H_2S drawn from *A*. Hydrogen sulphide water is obtained by opening the pinch cock *C* of the burette, the liquid drawn off being simultaneously replaced from the vessel II. The container is made of dark-colored glass to protect the hydrogen sulphide water from light. Water may be drawn into II, when required by opening the pinch cock leading to the bottle I.

strongly ignited, forming in presence of oxygen the stable magnesium pyroarsenate, $Mg_2As_2O_7$, in which form arsenic is determined.

Procedure. The solution containing the arsenic, in the form of arsenate, and having a volume not exceeding 100 cc. per 0.1 gram arsenic present, is treated with 5 cc. of concentrated hydrochloric acid, added, with constant stirring, drop by drop. Now 7 cc. to 10 cc. of magnesia mixture are added (55 grams $MgCl_2$+70 grams NH_4Cl+650 cc. H_2O and made up to 1000 cc. with NH_4OH, sp.gr. 0.96), for each 0.1 gram of arsenic present. A 10% ammonia solution is added from a burette, with stirring, until the mixture is neutralized (a red color imparted to the solution in presence of phenolphthalein indicator), and

[1] J. F. Virgili, Z. anal. Chem., **44**, 504 (1905).

then ammonia added in excess equal to one-third the volume of the neutralized solution. The precipitate is allowed to settle at least twelve hours and is then filtered into a weighed Gooch crucible and washed with 2.5% ammonia until free from chloride. After draining as completely as possible by suction the

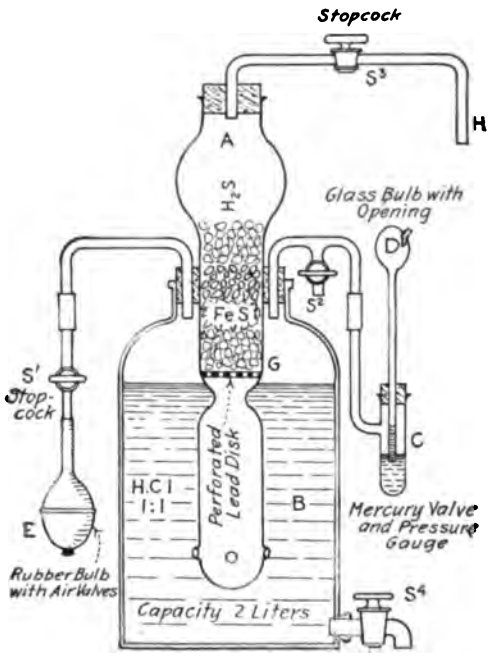


FIG. 3.—Scott's Hydrogen Sulphide Generator.

Fig. 3 shows a convenient form of a generator for obtaining hydrogen sulphide gas under pressure. The apparatus is the writer's modification of the Banks' generator shown in Fig. 4, and is designed for large quantities of hydrogen sulphide gas. The cylinder *A A'* is constricted, as shown, to support perforated lead disk *G*, upon which rests the iron sulphide. The lower end of the chamber is closed to catch small particles of FeS that may be carried through the perforations of the disk. Small openings admit the acid to *A'*. The level of the acid is below the disk *G*, so that the acid only comes in contact with the sulphide when pressure is applied by means of the rubber bulb *E*, the stopcock S^1 being open and S^2 closed. The mercury gauge *C* is adjusted to blow out at a given pressure, to prevent accident, the bulb *D* preventing the mercury from being blown out of the apparatus. A small opening in *D* allows the escape of the gas. When the apparatus is in operation, *H* is connected to an empty heavy-walled bottle, which in turn is attached with glass tube connection to the pressure flask in which the precipitation of the sulphide is made, the flask being closed to the outside air. By pressure on the rubber bulb *E*, acid is forced into the chamber *A'* past the disk into the sulphide in *A*. The entire system will now be under the pressure indicated by the gauge *C*. The pressure is released by opening the stopcock S^2 and the flask containing the precipitate then disconnected. The reservoir is designed to hold about two liters of acid, and the cylinder containing the sulphide is of sufficient capacity to hold over one pound of FeS, so that the apparatus will deliver a large quantity of hydrogen sulphide.

precipitate is dried at 100° and then heated to a dull red heat (400 to 500° C.), preferably in an electric oven, until free of ammonia. The temperature is then raised to a bright red heat (800 to 900° C.) for about ten minutes, the crucible then cooled in a desiccator and the residue weighed as $Mg_2As_2O_7$.

Factors, $Mg_2As_2O_7 \times 0.4827 = As$, or $\times 0.6373 = As_2O_3$, or $\times 0.7403 = As_2O_5$, or $\times 0.7925 = As_2S_3$.

NOTES. In place of an electric furnace the Gooch crucible may oe placed in a larger non-perforated crucible, the bottom of the Gooch being 2–3 mm. above the bottom of the outer crucible. The product may now be heated in presence of a current of oxygen passed through a perforation in the covering lid of the Gooch, or

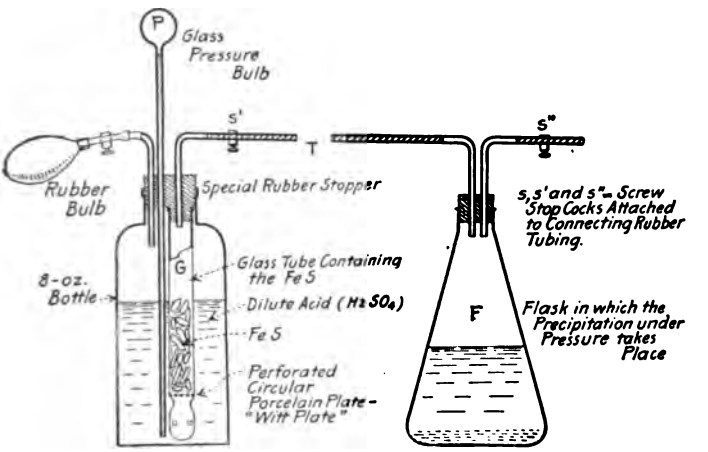


FIG. 4.—Banks' Hydrogen Sulphide Generator.

Fig. 4 shows a simple and effective pressure generator, designed by Banks. The operation of this small generator (200 cc. capacity) is similar to the apparatus described. It is especially adapted for laboratory work, where individual apparatus is desired for students in qualitative and quantitative analysis.

in place of the oxygen, a thin layer of powdered NH_4NO_3 may be placed on the arsenate residue and the heat gradually applied until the outer crucible attains a light red glow.

VOLUMETRIC METHODS FOR THE DETERMINATION OF ARSENIC

Oxidation of the Arsenous Acid with Standard Iodine [1]

This procedure is applicable for the determination of arsenic in acids, after reduction of arsenic to its arsenous form, for valuation of arsenic in the trioxide, for determination of arsenic isolated by distillation as arsenous chloride, for arsenic in arsenites and reduced arsenates in insecticides, etc. The method depends upon the reaction—$As_2O_3+2H_2O+2I_2=As_2O_5+4HI$. The liberated hydriodic acid is neutralized by sodium bicarbonate. The trace of excess iodine is detected by means of starch, a blue color being produced.

Procedure. If the solution is acid, it is neutralized by ammonium hydroxide or potassium carbonate (phenolphthalein indicator) then made slightly acid. If the solution is alkaline, it is made slightly acid. Two to 3 grams of sodium bicarbonate are added together with starch indicator and the solution titrated with tenth normal iodine solution, the iodine being added cautiously from a burette until a permanent blue color develops.

[1] Mohr's Method.

One cc. N/10 iodine = 0.00375 gram As, or 0.004948 gram As_2O_3.
$As_2O_3 \times 1.1616 = As_2O_5$. $As \times 1.3201 = As_2O_3$ or $\times 1.5336 = As_2O_5$.
$As_2O_3 \times 0.7575 = As$.

Volumetric Determination of Arsenic by Precipitation as Silver Arsenate

Bennett's modification of Pearce's method, combining Volhard's, depends upon precipitation of arsenic, from a solution neutralized with acetic, by addition of neutral silver nitrate solution; the silver arsenate is dissolved in nitric acid, and the silver titrated with standard thiocyanate.

Procedure. 0.5 gram, or less, of the finely powdered substance is fused with 3 to 5 grams of a mixture of sodium carbonate and potassium nitrate (1 : 1) about one-third being used on top of the charge. The cooled mass is extracted with boiling water and filtered. The filtrate, containing the alkali arsenate, is strongly acidified with acetic acid, boiled to expel the carbon dioxide, then cooled and treated with sufficient sodium hydroxide solution to give an alkaline reaction to phenolphthalein indicator. The purple red color is now discharged from the solution by addition of acetic acid. A slight excess of neutral silver nitrate is vigorously stirred in and the precipitate allowed to settle in the dark. The supernatant liquid is poured off through a filter and the precipitate washed by decantation with cold distilled water, then thrown on the filter and washed free of silver nitrate solution. The funnel is filled with water and 20 cc. of strong nitric acid added. The dissolved silver arsenate is caught in the original beaker in which the precipitation was made, the residue on the filter washed thoroughly with cold water and the filtrate and washings made up to 100 cc. The silver is now titrated by addition of standard ammonium or potassium thiocyanate, until a faint red color is evident, using ferric ammonium alum indicator, according to the procedure described for determination of silver. (See Chlorine and Silver Chapters.)

One cc. N/10 thiocyanate = 0.010788 gram Ag.
Factor. $Ag \times 0.2316 = As$.

NOTE. The silver arsenate salt is nearly six times the weight of arsenic, so that very small amounts of arsenic may be determined by the procedure, hence it is not necessary to use over 0.5 gram of the material. For traces of arsenic the Gutzeit method, following, should be used.

DETERMINATION OF SMALL AMOUNTS OF ARSENIC

Modified Gutzeit Method [1]

The following procedure furnishes a rapid and accurate method for determination of exceedingly small amounts of arsenic ranging from 0.001 milligram to 0.5 milligram As_2O_5. It is more sensitive and less tedious than the Marsh test. The details, given below with slight modifications, have been carefully worked out in the laboratories of the General Chemical Company [1] and have proved exceedingly valuable in estimating small amounts of arsenic in acids, bases, salts, soluble arsenic in lead arsenate and zinc arsenite and other insecticides, traces of arsenic in food products, baking powders, canned goods, etc.

[1] Paper by W. S. Allen and R. M. Palmer General Chemical Company, presented before the Eighth International Congress of Applied, Chemistry.

The method depends upon the evolution of arsine by the action of hydrogen on arsenic compounds under the catalytic action of zinc, the reaction taking place either in alkaline or acid solutions. The evolved arsine reacts with mercuric chloride, forming a colored compound. From the length and intensity of the color stain the amount of arsenic is estimated by comparison with standard stains.

Arsine is evolved from an acid solution under definite conditions of acidity, amount of zinc used, temperature, strength of solution of mercuric chloride used in sensitizing the test-paper, size of apparatus, volume of solution, amount of iron accelerator, and of stannous chloride reducer, etc., conditions which have proven, by extended tests, to be most efficient. These conditions must be adhered to for reliable results. For example, variation of acidity and the amount of zinc will produce stains of variable length and intensity with equal amounts of arsenic, the stain being longer and less intense with the more rapid evolution of the gas. Likewise the greater the concentration of mercuric chloride on the sensitized paper, the shorter the length of the stain and the deeper its color.

Special Reagents. ***Standard Arsenic Solution.*** One gram of resublimed arsenous acid, As_2O_3, is dissolved in 25 cc. of 20% sodium hydroxide solution (arsenic-free) and neutralized with dilute sulphuric acid. This is diluted with fresh distilled water, to which 10 cc. of 95% H_2SO_4 has been added, to a volume of 1000 cc. Ten cc. of this solution is again diluted to a liter with distilled water containing acid. Finally 100 cc. of the latter solution is diluted to a liter with distilled water containing acid. One cc. of the final solution contains 0.001 milligram As_2O_3.

Standard Stains. Two sets of stains are made, one for the small apparatus for determining amounts of As_2O_3 ranging from 0.001 to 0.02 milligram, and a second set for the larger-sized apparatus for determining 0.02 to 0.5 milligram As_2O_3. Stains made by As_2O_3 in the following amounts are convenient for the standard sets; e.g., small apparatus, 0.001, 0.002, 0.004, 0.006, 0.01, 0.15, 0.02 milligram As_2O_3. Large apparatus, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 milligram As_2O_3.

In making the stain the requisite amount of standard reagent, As_2O_3 solution, is placed in the Gutzeit bottle with the amounts of reagents prescribed for the regular tests and the run made exactly as prescribed in the regular procedure.

Preservation of the Stains. The strips of sensitized paper with the arsenic stain are dipped in molten paraffine (free from water), and mounted on a sheet of white paper, folded back to form a cylinder. The tube is placed in a glass test-tube containing phosphorus pentoxide, which is then closed by a stopper. It is important to keep the stained strip dry, otherwise the stain soon fades, hence the paper on which the strips are mounted and the glass test-tube, etc., must be perfectly dry. It is advisable to keep the standard in a hydrometer case, while not in use, as light will gradually fade the color.

Sensitized Mercuric Chloride (or Bromide) Paper. 20×20 in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in the large Gutzeit apparatus the paper is dipped into a 3.5% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus it is dipped into a 0.5% mercuric chloride solution. (The weaker the solution, the longer and less intense will be the stain.) A squeegee roller is passed gently over the impregnated paper, placed on plate glass, to

remove the greater part of the reagent. The paper, placed on a clean cloth, is dried at a temperature of 100° C. Immediately upon drying it removed from the oven ($HgCl_2$ is slightly volatile with heat), half an inch the outer edge trimmed off, since this is apt to contain more of the reage and the paper cut into strips. The paper with more concentrated reag is cut into strips 13 cm. by 5 mm. and that with 0.5% mercuric chlor into strips 7 cm. by 4 mm. The paper is preserved in bottles with tight-fitti

FIG. 5.—Purification of Hydrochloric Acid.

stoppers. Standards should be made with each batch of paper. Paper wi a white deposit of $HgCl_2$ should not be used.

Ferric Ammonium Alum. Eighty-four grams of the alum with 10 cc. mixed acid is dissolved and made up to a liter. Ten cc. of this solution co tains approximately 0.5 gram Fe_2O_3.

Lead Acetate. One per cent solution with sufficient acetic acid to cl the solution.

Zinc. Arsenic-free zinc shot, 3 to 6-in. mesh. The zinc is treated with C. hydrochloric acid, until the surface of the zinc becomes clean and dull. It

then washed and kept, in a casserole, covered with distilled water, a clock-glass keeping out the dust.

Mixed Acid. One volume of arsenic-free H_2SO_4 is diluted with four volumes of pure water and to this are added 10 grams of NaCl dissolved in 100 cc. of water.

Stannous Chloride. Eighty grams of stannous chloride dissolved in 100 cc. of water containing 5 cc. arsenic-free hydrochloric acid (1.2 sp.gr.).

Arsenic-free Hydrochloric Acid. The commercial acid is treated with potassium chlorate to oxidize the arsenic to its higher form and the acid distilled. The distilling apparatus may be arranged so that a constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chlorate, fresh hydrochloric acid being supplied as rapidly as the acid distills. See Fig. 5 on page 42.

Lead Acetate Test Paper for Removal of H_2S. Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips 7×5 cm.

Blanks should be run on all reagents used for this work. The reagents are arsenic-free if no stain is produced on mercuric chloride paper after forty-five minutes' test.

Special Apparatus. The illustration, Fig. 6 (page 46), shows the Gutzeit apparatus connected up, ready for the test. The dimensions on the left-hand side are for the small apparatus and those on the right for the large form. Rubber stoppers connect the tubes to the bottle. The apparatus consists of a wide-mouth 2-oz. or 8-oz. bottle according to whether the small or large apparatus is desired, two short glass tubes containing dry lead acetate paper and moist glass wool for removal of traces of hydrogen sulphide and a small-bore tube containing the strip of mercuric chloride paper.

Preparation of the Sample

The initial treatment of the sample is of vital importance to the Gutzeit Method for determining traces of arsenic. The following procedures cover the more important materials or substances in which the chemist will be called upon to determine minute amounts of arsenic.

Traces of Arsenic in Acids. The acid placed in the Gutzeit apparatus should be equivalent to 4.2 grams of sulphuric acid or 3.1 grams of hydrochloric acid and should contain 0.05 to 0.1 gram Fe_2O_3 equivalent. If large samples are required for obtaining the test it is necessary either to expel a portion of the acid in order to obtain the above acidity or to make standard stains under similar conditions of acidity. It must be remembered that arsenous chloride is readily volatile, whereas the arsenic chloride is not, hence it is necessary to oxidize arsenic before attempting to expel acids. If nitric acid or bromine or chlorine (chlorate) be added for this purpose, it must be expelled before attempting the Gutzeit test. Nitric acid may be expelled by adding sulphuric acid and taking to SO_3 fumes. Free chlorine, bromine, or iodine will volatilize on warming the solution. Chlorine in a chlorate is expelled by taking the sample to near dryness in presence of free acid. Sulphurous acid or hydrogen sulphide, if present, should be oxidized by addition of potassium permanganate in slight excess (faint pink color) the excess destroyed by a drop or so of oxalic acid. SO_2 is reduced by zinc and hydrogen to H_2S, which forms black HgS

with mercuric chloride, hence oxidation of SO_2 and H_2S are necessary before running the test.

Sulphuric Acid. With amounts of arsenic exceeding 0.00005% As_2O_3, 5 to 10 grams of acid, according to its strength, are taken for analysis and diluted to 15 or 20 cc. If H_2S or SO_2 are present, potassium permanganate solution is added until a permanent pink color is obtained and the excess destroyed by a drop or so of oxalic acid. In mixed acid containing nitric acid the sample is taken to SO_3 fumes to expel nitric acid. The procedure given later for the regular determination is now followed.

For estimating very minute amounts of arsenic, 0.000005 to 0.00005% As_2O_3, it is necessary to take a 25- to 50-gram sample for analysis. The acid is treated as directed above for removal of H_2S or SO_2 or nitric acid and diluted in the Gutzeit apparatus to at least 130 cc., using the large apparatus. Upon the addition of iron and stannous chloride as directed in the procedure the run is made with 25 pieces of zinc. The stains are compared with standard stains produced by known amounts of arsenic added to 50-gram portions of arsenic-free sulphuric acid of strength equal to that of the sample. The stains are longer and less intense than those produced by less acid.

Hydrochloric Acid. Twenty cc. is taken for analysis (sp.gr. being known); the sample should contain an acid equivalent of about 3.1 grams of hydrochloric acid. Chlorine is expelled by bubbling air through the acid before taking a sample. The procedure is given for further treatment of the sample following the section on preparation of the sample.

Nitric Acid. One hundred cc. of the acid (sp.gr. being known) is evaporated with 5 cc. of concentrated sulphuric acid to SO_3 fumes, to expel nitric acid. Arsenic is determined in the residue by the standard procedure.

Iron Ores, Pyrites, Burnt Pyrites, Cinders, etc. One gram of the finely ground ore is oxidized by treating with 5 cc. of a mixture of 2 parts liquid bromine and 3 parts of carbon tetrachloride. After fifteen minutes, 10 cc. of concentrated nitric acid are added and the mixture taken to dryness. Five cc. of concentrated sulphuric acid (95%) are added and the mixture taken to SO_3 fumes to expel the nitric acid. The cooled sample is taken up with 50 cc. of water and digested until all of the iron sulphate has dissolved; it is now washed into a 100-cc. flask, made to volume, and arsenic determined in an aliquot portion in the usual way, given later. Insoluble Fe_2O_3, briquettes, etc., is best dissolved by fusion with potassium bisulphate, $KHSO_4$. The fused mass is dissolved in warm dilute hydrochloric acid, and then washed into the Gutzeit bottle.

Alumina Ores. Bauxite. One gram of bauxite is treated with one part of concentrated nitric acid and 6 parts of concentrated hydrochloric acid, and taken to dryness on the water bath. The residue is taken up with an equivalent of 4.7 grams of hydrochloric acid or 6.3 grams of sulphuric acid in a volume of 25 cc. and the mix heated until the material has dissolved. The sample is diluted to exactly 100 cc. and arsenic determined on an aliquot portion.

Phosphates, Phosphoric Acid. Arsenic, in phosphoric acid, combined or free, cannot be determined in the usual way, as P_2O_5 has a retarding effect upon the evolution of arsine, so that the results are invariably low, and small amounts of arsenic escaping detection. Arsenic, however, may be volatilized from phosphates and phosphoric acid, as arsenous chloride, $AsCl_3$, in a current of

hydrogen chloride by heating to boiling. One gram or more of the phosphate is placed in a small distilling flask, connected directly to a 6-in. coil condenser dipping into the Gutzeit bottle, containing 20 to 30 cc. of cold distilled water. A second bottle connected in series may be attached for safeguarding loss (this seldom occurs). Fifty cc. of concentrated hydrochloric acid are added to the sample and 5 grams of cuprous chloride. Arsenic is distilled into the Gutzeit bottle by heating the solution to boiling and passing a current of air through strong hydrochloric acid into the distilling flask by applying suction at the receiving end of the system. All of the arsenic will be found in the first 10 or 15 cc. of the distillate. Arsenic may now be evolved after addition of iron, stannous chloride and zinc, as directed in the procedure.

Salts, Sodium Chloride, Magnesium Sulphate, etc. One-gram samples are taken and dissolved in a little water and an equivalent of 6.3 grams of sulphuric acid added. The solution of iron and stannous chloride having been added, the run is made with 25 pieces of zinc, placed in the Gutzeit bottle.

Baking Powder, Other than Phosphate Baking Powder. A ten-gram sample is heated with 10 cc. hydrochloric acid, 10 cc. of ferric ammonium alum and 30 cc. of distilled water, until the starch hydrolyzes. 0.5 cc. of stannous chloride is added to the hot solution and the mixture washed into the Gutzeit apparatus. Twenty-five pieces of zinc are added and the arsenic determined as usual.

Phosphate Baking Powders. Ten grams of the material mixed to a paste with about 50 cc. of hydrochloric acid are transferred to a small distilling flask with a few cc. of HCl. A tube, connected to a bottle of strong hydrochloric acid, passes into the mixture in the flask through a ground glass stopper. The flask is attached to a tube, which dips into water in a Gutzeit bottle. Two grams of cuprous chloride are added, the apparatus made tight and the flask immersed in boiling hot water. By aspirating air through the system into the Gutzeit bottle, which is water cooled, arsenic distills into the bottle and may be determined by the procedure outlined.

Arsenic in Organic Matter, Canned Goods, Meat, etc. The finely chopped, well-mixed sample is placed in a large flask and enough water added to produce a fluid mass. An equal quantity of concentrated hydrochloric acid and 1 to 2 grams of potassium chlorate are added. The flask is shaken to mix the material and it is then placed on the steam bath. Upon becoming hot, nascent chlorine is evolved and vigorously attacks the organic matter. Half-gram portions of potassium chlorate are added at five-minute intervals, shaking the flask frequently. When the organic material has decomposed and the solution becomes a pale yellow color, the mass is diluted with water and filtered. Arsenic will be found in the filtrate. A white, amorphous substance generally remains on the filter, when cadaver is being examined. The filtrate is diluted to a given volume and an aliquot portion taken for analysis. This is evaporated to near dryness to expel excess of acid and decompose chlorates. An equivalent of 4.7 grams of hydrochloric acid is added (three times this amount for the large apparatus), the volume of the solution made to about 30 cc., 10 cc. of ferric ammonium alum and 0.5 cc. of stannous chloride added, and the solution poured into the Gutzeit apparatus for the test as given below.

Procedure for Making the Test

For amounts of arsenic varying from 0.001 milligram to 0.02 milligram As_2O_3, the small apparatus is used. The volume of the solution should be 50 cc. It should contain an equivalent of 4.2 to 6.3 grams sulphuric acid and should have about 0.1 gram equivalent of Fe_2O_3 reduced by 0.5 cc. of stannous chloride solution. Arsine is generated by adding 12 to 25 pieces of zinc.

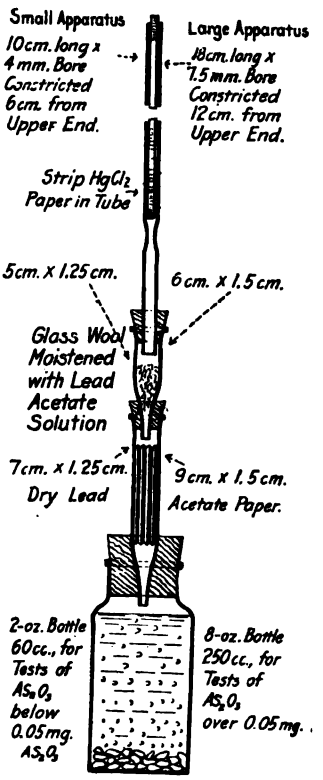

Small Apparatus
10cm. long x 4 mm. Bore Constricted 6cm. from Upper End.
Large Apparatus
18cm. long x 7.5 mm. Bore Constricted 12cm. from Upper End.
Strip $HgCl_2$ Paper in Tube
5cm. x 1.25cm.
6cm. x 1.5cm.
Glass Wool Moistened with Lead Acetate Solution
7cm. x 1.25cm. Dry Lead
9cm. x 1.5cm. Acetate Paper.
2-oz. Bottle 60cc., for Tests of As_2O_3 below 0.05mg. As_2O_3
8-oz. Bottle 250cc., for Tests of As_2O_3 over 0.05mg.

FIG. 6.—Gutzeit Apparatus for Arsenic Determination.

For amounts ranging from 0.02 to 0.5 milligram As_2O_3, the large apparatus is used. The volume of the solution should be about 200 cc. and should contain an equivalent of 18.5 grams of sulphuric acid and should have 0.1 gram equivalent of Fe_2O_3, reduced by 0.5 cc. stannous chloride solution. Arsine is generated by adding 25 to 40 pieces of arsenic-free zinc. The temperature should be 105° F. The sample taken should be of such size that a stain is obtained equivalent to that given by 0.1 to 0.5 milligram As_2O_3.

Lead acetate paper is placed in the tube next to the bottle; the middle tube (see Fig. 6) contains glass wool moistened with lead acetate solution; the upper tube contains the test strip of mercuric chloride paper. Immediately upon adding the required amount of zinc to the solution in the bottles, the connected tubes are put in position, as shown in the illustration, and the bottle gently shaken and allowed to stand for thirty minutes for the small apparatus, forty minutes for the large. The test paper is removed, dipped in molten paraffine and compared with the standard stains. See Plate I.

Estimation of Per cent.

$$\frac{\text{The milligram } As_2O_3 \text{ stain} \times 100}{\text{Weight of sample taken}} = \%\ As_2O_3.$$

NOTES. Ferrous iron prevents polarization between zinc and the acid and hence aids in the evolution of arsine.

In the analysis of baking powders, bauxite, sodium or similar salts, additional zinc—25 pieces, and additional acid, 6.3 grams sulphuric acid equivalent, are required.

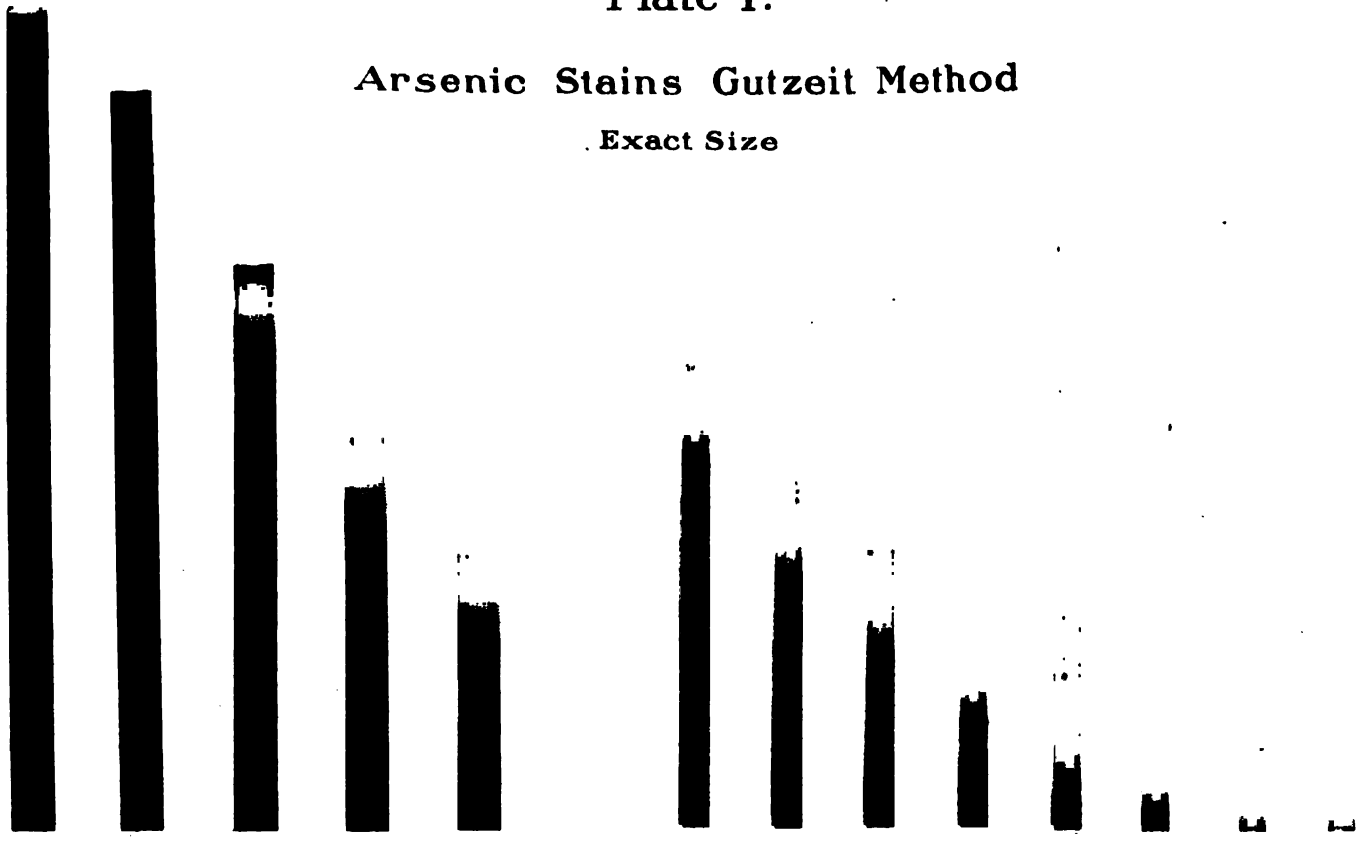
Hydrochloric acid is used in place of sulphuric acid in cases where complete solution by the latter acid cannot be effected.

Standards and samples should be run under similar conditions, temperature, acidity, amount of zinc, volume of solution, etc.

Plate I.

Arsenic Stains Gutzeit Method

Exact Size



Large Gutzeit Apparatus

Small Gutzeit Apparatus

The numerals represent milligrams As_2O_3 causing the stain

METHOD FOR ANALYSIS OF COMMERCIAL "ARSENIC," ARSENOUS OXIDE, As_2O_3

The following constituents may be commonly present as impurities, SiO_2, Sb_2O_3, Fe_2O_3, NiO, CoO, CaO, SO_3, Cu, Pb, and Zn.

Determination of Moisture

Two 10-gram samples are dried to constant weight in the oven at 100° C. Loss in weight = moisture.

Sulphuric Acid, H_2SO_4

The samples from the moisture determination are dissolved in concentrated hydrochloric acid, heating to boiling if necessary, and the samples diluted to 300 to 400 cc. Barium chloride solution is added in slight excess to the hot solution, the precipitate, $BaSO_4$, allowed to settle and filtered and the sulphate dried and ignited as usual.

$$BaSO_4 \times 0.343 = SO_3.$$

Determination of Arsenic as As_2O_3

Duplicate 5-gram samples are dissolved in 20 grams potassium carbonate in 60 cc. of hot water, by boiling until solution is effected. The samples are made up to 1 liter and aliquots of 100 cc. (=0.5 gram) taken for analysis. The solution is made faintly acid with hydrochloric acid, testing the solution with litmus paper or by adding methyl orange directly to the solution. An excess of bicarbonate is added and the arsenic titrated with tenth-normal iodine according to the standard procedure for arsenic. One cc. N/10 I = .004948 gram As_2O_3.

Residue upon Sublimation of As_2O_3. SiO_2, Pb, Cu, Fe_2O_3, NiO, CoO, Zn

Two 5-gram samples are weighed into tared porcelain crucibles and heated gently on sand baths with the sand banked carefully around the crucible so as to heat the entire receptacle. After the greater part of the arsenous oxide has volatilized, the crucible is ignited directly in the flame to a dull red heat, until fumes are no longer given off. The residue is weighed as total non-sublimable residue.

Silica

The residues are transferred to beakers and treated with aqua regia, taken to dryness, and the silica dehydrated at 110° C. for an hour or more. The residue is taken up with hot dilute hydrochloric acid, boiled, and the silica filtered off, ignited, and weighed.

Lead and Copper

The filtrate from the silica is "gassed" with H_2S and the precipitate filtered off. The filtrate is put aside for determination of iron, etc. The precipitate is dissolved in hot dilute nitric acid, 2 to 3 cc. of concentrated sulphuric acid added,

the solution taken to SO_3 fumes, the cooled concentrate diluted to 20 or 30 cc. and the lead sulphate filtered off, ignited, and weighed as $PbSO_4$.

The filtrate from the lead sulphate containing the copper is treated with aluminum powder and the copper thrown out of solution; the excess of aluminum is dissolved with a few cc. of hydrochloric acid. The filtrate should be tested for copper with H_2S and the precipitate added to the copper thrown out by the aluminum. The copper on the filter is dissolved in hot dilute nitric acid, the extract evaporated to 2 or 3 cc., the acid neutralized with ammonia and then made acid with acetic, potassium iodide added and the liberated iodine titrated with standard thiosulphate solution according to the regular scheme for copper.

Iron, Nickel, Cobalt, and Zinc

The filtrate from the H_2S Group is boiled to expel the H_2S and the iron oxidized by addition of nitric acid and boiling. The iron (and alumina) is precipitated with ammonium hydroxide and the precipitate filtered off and washed several times with hot water. If alumina is suspected (light-colored precipitate) it may be determined by the difference method—ignition of the precipitate, weighing, and finally subtracting the iron found by titration with standard stannous chloride solution. The iron is dissolved in hydrochloric acid and titrated hot with stannous chloride solution.

The filtrate from the iron is boiled and a 1% alcoholic solution of dimethylglyoxime added to precipitate the nickel. The salt is filtered on a tared Gooch, the precipitate dried at 100° C., and weighed. The weight of the salt $\times 0.2032 = Ni$.

The filtrate from the nickel is boiled until all the alcohol has been driven off and the cobalt precipitated by addition of sodium hydroxide in excess filtered, ignited, and weighed as CoO.

The filtrate is made acid with hydrochloric acid, and then alkaline with ammonium hydroxide and colorless sodium sulphide solution added to precipitate the zinc. The mixture is boiled five to ten minutes, the precipitated ZnS allowed to settle, filtered off, and washed once or twice and then dissolved in hydrochloric acid and the zinc determined by titration directly with potassium ferrocyanide, or by converting to the carbonate by addition of potassium carbonate, filtered and washed free of alkali, the precipitate dissolved in a known amount of standard acid, and the excess acid titrated with standard caustic (methyl orange indicator) according to the procedure given for zinc. $H_2SO_4 \times 0.06665 = Zn$.

Antimony and Calcium Oxides

Two 15-gram samples are treated with 300 cc. of concentrated hydrochloric acid, boiled down to 50 cc. to expel the arsenic as $AsCl_3$, an equal amount of concentrated hydrochloric acid is added, and the last traces of arsenic precipitated by H_2S passed into the hot concentrated hydrochloric acid solution. The arsenous sulphide, As_2S_3, is filtered off. Antimony is precipitated by diluting the solution with an equal volume of water, the solution having been concentrated by boiling down to about 50 cc. The Sb_2S_3 is filtered off, washed several times with hot water, dissolved by washing through the filter with concentrated hydrochloric acid, and antimony determined in the strong hydrochloric acid solution by the potassium bromate method—addition of methyl orange indicator

and titration with standard potassium bromate added to the hot solution to the disappearance of the pink color of the indicator.

The filtrate from the antimony is concentrated, made slightly alkaline with ammonium hydroxide, and gased with hydrogen sulphide to remove iron, nickel, cobalt, zinc, chromium, and last traces of lead, etc. The filtrate is then concentrated and made acid with crystals of oxalic acid, boiled and methyl orange added and then ammonia drop by drop slowly until the indicator changes to an orange color. An excess of ammonium oxalate is now added and the beaker placed on the steam bath until the calcium oxalate has settled. The lime is now determined by filtering off the precipitate and washing, drying and igniting to CaO, or by titration with standard permanganate, according to the regular procedure for calcium.

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BARIUM

WILFRED W. SCOTT

Ba, *at.wt.* 137.37; *sp.gr.* 3.78; *m.p.* 850° C.; *volatile at* 950° C.; *oxides*, BaO, BaO_2.

DETECTION

Barium is precipitated as the carbonate together with strontium and calcium, by addition of ammonium hydroxide and ammonium carbonate to the filtrate of the ammonium sulphide group. It is separated from strontium and calcium by precipitation as yellow barium chromate, $BaCrO_4$, from a slightly acetic acid solution.

Saturated solutions of calcium or strontium sulphates precipitate white barium sulphate, $BaSO_4$, from its chloride or nitrate or acetate solution, barium sulphate being the least soluble of the alkaline earth sulphates.

Soluble chromates precipitate yellow barium chromate from its neutral or slightly acetic acid solution, insoluble in water, moderately soluble in chromic acid, soluble in hydrochloric or nitric acid.

Fluosilicic acid, H_2SiF_6, precipitates white, crystalline barium fluosilicate, $BaSiF_6$, sparingly soluble in acetic acid, insoluble in alcohol. (The fluosilicates of calcium and strontium are soluble.)

Flame. Barium compounds color the flame yellowish green, which appears blue through green glass.

Spectrum.[1] Three characteristic green bands (α, β, γ).

Barium sulphate is precipitated by addition of a soluble sulphate to a solution of a barium salt. The compound is extremely insoluble in water and in dilute acids (soluble in hot concentrated sulphuric acid). The sulphate is readily distinguished from lead sulphate by the fact that the latter is soluble in ammonium salts, whereas barium sulphate is practically insoluble.

ESTIMATION

The determination of barium is required in the valuation of its ores, barite, heavy spar, $BaSO_4$; witherite, $BaCO_3$; baryto calcite, $BaCO_3CaCO_3$. It is determined in certain white mixed paints and colored pigments, Venetian, Hamburg or Dutch whites, chrome paints, etc. In analysis of Paris green, baryta insecticides, putty, asphalt, dressings and pavement surfacings. It may be found as an adulterant in foods, wood preservatives, filler in rubber, rope, fabrics. It is determined in salts of barium. The nitrate is used in pyrotechny, in mixtures for green fire.

Preparation and Solution of the Sample

Compounds of barium, with the exception of the sulphate, $BaSO_4$, are soluble in hydrochloric and nitric acids. The sulphate is soluble in hot concen-

[1] See Preliminary Tests under Separations.

trated sulphuric acid, but is reprecipitated upon dilution of the solution. The sulphate is best fused with sodium carbonate, which transposes the compound to barium carbonate; sodium sulphate may now be leached out with water and the residue, $BaCO_3$, then dissolved in hydrochloric acid.

Solution of Ores. Sulphates. 0.5 to 1 gram of the finely divided ore is fused with 3 to 5 grams of sodium and potassium carbonate mix, 2 : 1, or sodium carbonate alone, in a platinum dish. (Prolonged fusion is not necessary.) The melt is cooled and then extracted with hot water to dissolve out the alkali sulphates. Barium carbonate, together with the other insoluble carbonates, may now be dissolved by hot dilute hydrochloric acid. From this solution barium may be precipitated by addition of sulphuric acid. If it is desired to separate barium along with strontium, calcium, and magnesium, the members of the preceding groups are removed by H_2S in acid and in ammoniacal solution, as directed under "Separations."

Sulphides. The ore is oxidized, as directed for pyrites under the subject of sulphur. After the removal of the soluble sulphates, the residue, containing silica, barium, and small amounts of insoluble oxides, is fused and dissolved according to the procedure for sulphates.

Carbonates. In absence of sulphates the material may be dissolved with hydrochloric acid, taken to dryness to dehydrate silica and after heating for an hour in the steam oven (110°±) the residue is extracted with dilute hydrochloric acid and filtered. The filtrate is examined for barium according to one of the procedures given later.

Salts Soluble in Water. Nitrates, chlorides, acetates, etc., are dissolved with water slightly acidulated with hydrochloric acid.

Material Containing Organic Matter. The substance is roasted to destroy organic matter before treatment with acids or by fusion with the alkali carbonates.

The Insoluble Residue remaining from the acid treatment of an ore may contain barium sulphate in addition to silica, etc. The filter containing this residue is burned and the ash weighed. Silica is now volatilized by addition of hydrofluoric acid with a few drops of sulphuric acid, and evaporation to dryness. If an insoluble substance still remains after taking up the remaining residue with dilute hydrochloric acid, barium sulphate is indicated. This is treated according to the method given for sulphates.

NOTE. The insoluble substance remaining is frequently ignited and weighed as barium sulphate without fusion with the carbonate.

SEPARATIONS

The Alkaline Earths

Preliminary Considerations. In the determination of barium, calcium, and strontium, the following causes may lead to loss of the elements sought:

a. Presence of Phosphates. Phosphoric acid, free or combined, has a decided influence upon the determination of the members of this group. Combined as phosphate it will cause the complete precipitation of barium, calcium, and strontium, along with iron, alumina, etc., upon making the solution alkaline for removal of the ammonium sulphide group. It is a common practice to hold up the iron+alumina by means of tartaric, citric, or other organic acids before making ammoniacal for precipitation of this group as oxalates, or again the basic acetate method is used for precipitation of iron and alumina; calcium,

barium, and strontium going into solution. These procedures may be satisfactory for the analysis of phosphate rock and similar products, but do not cope with the difficulty when large amounts of phosphates are present. In samples containing free phosphoric acid, barium, calcium, and strontium, present in small amounts, may remain in solution in presence of sulphates or oxalates. Appreciable amounts of calcium, 1% or more, may escape detection by the usual method of precipitation by ammonium oxalate added to the alkaline solution, on account of this interference, so that the removal of phosphoric acid before precipitation of this group is frequently necessary. This may be accomplished by addition of potassium carbonate in sufficient excess to combine completely with the phosphoric acid and form carbonates with the bases. The material taken to dryness is fused with additional potassium carbonate in an iron crucible, and the fusion leached with hot water—sodium phosphate dissolves and the carbonates of the heavy metals remain insoluble.

b. Another source of loss is the presence of sulphates, either in the original material or by intentional or accidental addition, in the latter case due to the oxidation of hydrogen sulphide, which has been passed into the solution during the removal of elements of the hydrogen sulphide and ammonium sulphide groups, barium and strontium sulphate being precipitated along with these members. A potassium carbonate fusion will form Na_2SO_4, which may be leached out with water.

c. Loss may be caused by occlusion of barium, calcium, strontium, and magnesium by the gelatinous precipitates $Fe(OH)_3$, $Al(OH)_3$, etc. A double precipitation of these compounds should be made if considerable amounts are present.

d. A large excess of ammonium salts, which accumulate during the preliminary separations, will prevent precipitation of the alkaline earths. This can be avoided by using the necessary care required for accurate work, the addition of reagents by means of burettes or according to definite measurements in graduates, etc. Careless addition of large amounts of ammonium hydroxide and hydrochloric acid should be guarded against. In case large amounts of ammonium chloride are present, time is frequently saved by a repetition of the separations. Ammonium chloride may be expelled by heating the material, taken to dryness in a large platinum dish, the ammonium salts being volatilized.

e. Carbon dioxide absorbed by ammonium hydroxide from the air will precipitate the alkaline earths with the ammonium sulphide group.

Direct Precipitation on Original Sample. For the determination of barium, calcium, and strontium, it is advisable to take a fresh sample, rather than one that has been previously employed for the estimation of the hydrogen sulphide and ammonium sulphide groups, as is evident from the statements made above. The alkaline earths are isolated by being converted to the insoluble sulphates and separations effected as given later under Sulphate Method.

Preliminary Tests. Much time may be saved by making a preliminary test for barium, strontium, and calcium by means of the spectroscope and avoiding unnecessary separations. By this means one-thousandth of a milligram of barium, six hundred-thousandths of a milligram of strontium or calcium may be detected. The characteristic spectra of these elements are given in the chart. Plate II.

By means of the spectroscope with the use of the ordinary Bunsen flame 0.2 milligram of calcium, 0.6 milligram of strontium and 14 milligrams of barium

Emmissions-Spectra.

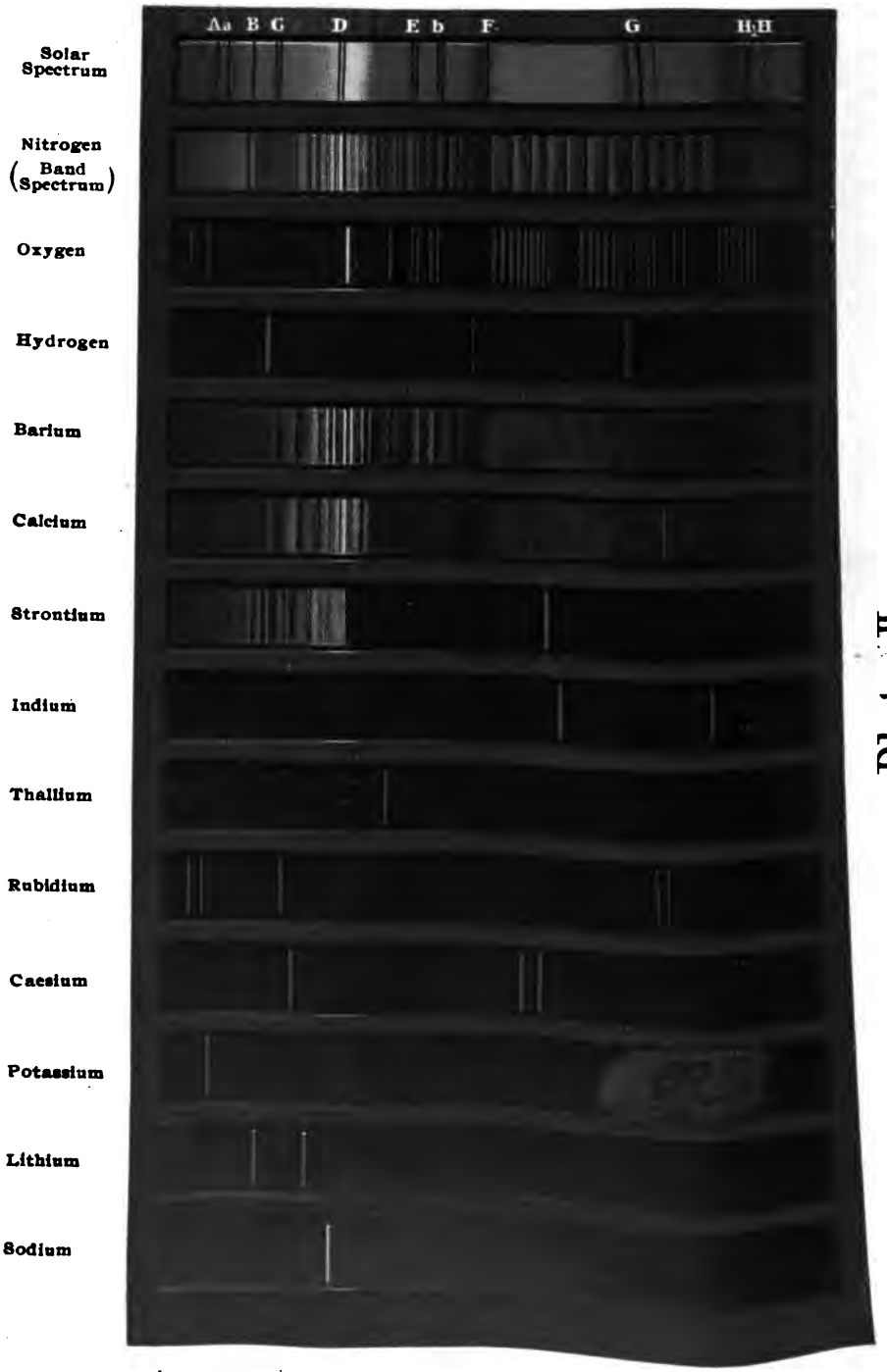

Plate II.

may be detected per cc. The test is very much more delicate by the arc spectra method.[1] The liquid containing the substance is connected to the positive pole and an iridium needle is connected by means of an adjustable resistance of 300 to 500 ohms to the negative pole. An E.M.F. of 100 to 200 volts and 1 ampere current are required. By the arc it is possible to detect 0.002 milligram of calcium, 0.003 milligram of strontium, 0.006 milligram of barium, 0.1 milligram of magnesium per cc. In these concentrations, calcium shows one brilliant line (423 $\mu\mu$), a bright line (616 $\mu\mu$), and a faint line between them; strontium two bright lines (422 and 461 $\mu\mu$) and two fairly bright lines; barium two brilliant lines (455 and 493 $\mu\mu$), two other bright lines, and a fairly bright one; and magnesium a brilliant band composed of three lines (516.8 to 518.4 $\mu\mu$), as well as a fairly bright line further towards the violet end of the spectrum.

The flame test may be of value in absence of sodium; barium giving a green flame, strontium a brilliant scarlet, and calcium an orange red.

Separation from Members of Previous Groups. The members of the previous groups may be removed by precipitation as sulphides by H_2S passed into the acid and then the alkaline solutions, the combined filtrates concentrated to about 300 cc. and made slightly acid with hydrochloric acid. The following procedures for isolation of barium from magnesium and the alkalies and from members of the alkaline earth group may be necessary before precipitation in its final form. The methods of separation will apply to the analyses of the elements mentioned so that the details of procedure will not be given elsewhere.

Separation of the Alkaline Earths from Magnesium and the Alkalies. Two general procedures will cover conditions commonly met with in analytical work:

A. Oxalate Method. Applicable in presence of comparatively large portions of calcium. The acid solution containing not over 1 gram of the mixed oxides is brought to a volume of 350 cc. and for every 0.1 gram of magnesium present about 1 gram of ammonium chloride is added, unless already present. Sufficient oxalic acid is added to completely precipitate the barium, calcium, and strontium.[2] ($H_2C_2O_4 \cdot 2H_2O = 126.04$, $Ba = 137.37$, $Ca = 40.07$, $Sr = 87.63$.) The solution is slowly neutralized by addition, drop by drop, of dilute ammonium hydroxide (1 : 10), methyl orange being used as indicator. About ½ gram of oxalic acid is now added in excess, the solution again made alkaline with ammonium hydroxide, and allowed to settle for at least two hours. The precipitate is filtered off and washed with water containing 1% ammonium oxalate, faintly alkaline with ammonia.

The precipitate contains all the calcium and practically all of the barium and strontium. If Mg is present in amounts of 10 to 15 times that of the alkaline earths a double precipitation is necessary, to remove it completely from this group. The oxalates are dissolved in hydrochloric acid and reprecipitated with ammonium oxalate in alkaline solution.

The filtrate contains magnesium and the alkalies. Traces of barium and strontium may be present. If the sample contains a comparatively large proportion of barium and strontium, the filtrate is evaporated to dryness, the ammonium salts expelled by gentle ignition of the residue, and the Ba and

[1] E. H. Riesenfeld and G. Pfützer, Ber., 1913, **46**, 3140–3144; Analyst, 1913, **38**, 584.

[2] Calcium and strontium will slowly precipitate in the oxalic acid solution. Ba oxalate will precipitate upon making the solution alkaline.

Sr recovered as sulphates according to the method described below. Magnesium is precipitated as magnesium ammonium phosphate from the filtrate.

The oxalates of barium, calcium, and strontium are ignited to oxides, in which form they may be readily converted to chlorides by dissolving in hydrochloric acid, or to nitrates by nitric acid.

B. Sulphate Method. Applicable in presence of comparatively large proportions of barium, strontium, or magnesium. The solution containing the alkaline earths, magnesium and the alkalies is evaporated to dryness and about 5 cc. concentrated sulphuric acid added, followed by 50 cc. of 95% alcohol. The sulphates [1] of barium, calcium, and strontium, are allowed to settle, and then filtered onto an S. and S. No. 589 ashless filter paper and washed with alcohol until free of magnesium sulphate. In presence of large amounts of magnesium as in case of analyses of Epsom salts and other magnesium salts it will be necessary to extract the precipitate by adding a small amount of water, then sufficient 95% alcohol to make the solution contain 50% alcohol and filter from the residue. Magnesium is determined in the filtrate.

The residue containing barium, calcium, and strontium as sulphate is fused with 10 parts of potassium carbonate or sodium acid carbonate until the fusion becomes a clear molten mass, a deep platinum crucible being used for the fusion. A platinum wire is inserted and the mass allowed to solidify. The fusion may be removed by again heating until it begins to melt around the surface next to the crucible, when it may be lifted out on the wire. The mass is extracted with hot water and filtered, Na_2SO_4 going into the solution and the carbonates of barium, strontium, and calcium remaining insoluble. The carbonates should dissolve completely in hydrochloric acid or nitric acid, otherwise the decomposition has not been complete, and a second fusion of this insoluble residue will be necessary.

Separation of the Alkaline Earths from One Another. This separation may be effected by either of the following processes:

1. Barium is separated in acetic acid solution as a chromate from strontium and calcium; strontium is separated as a nitrate [2] from calcium in ether-alcohol or amyl alcohol.

2. The three nitrates are treated with ether-alcohol in which barium and strontium nitrates are insoluble and calcium dissolves; the barium is now separated from strontium by ammonium chromate.

Procedures. 1. (a) Separation of Barium from Strontium (and from Calcium). In presence of an excess of ammonium chromate, barium is precipitated from solutions, slightly acid with acetic acid, as barium chromate (appreciably soluble in free acetic acid), whereas strontium and calcium remain in solution.

The mixed oxides or carbonates are dissolved in the least amount of dilute hydrochloric acid and the excess of acid expelled by evaporation to near dryness. The residue is taken up in about 300 cc. of water and 5–6 drops of acetic acid (sp.gr. 1.065) together with sufficient ammonium acetate (30% solution) to neutralize any free mineral acid present. The solution is heated and an excess of ammonium chromate (10% neutral sol.) [3] added (10 cc. usually sufficient).

[1] Solubility of $BaSO_4$ = 0.17 milligram, $CaSO_4$ = 179 milligram, $SrSO_4$ = 11.4 milligrams per 100 cc. sol. cold.

[2] Method of Stromayer and Rose. H. Rose, Pogg. Ann., **110**, 292, (1860).

[3] The solution is prepared by adding NH_4OH to a solution of $(NH_4)_2Cr_2O_7$ until yellow. The solution should be left acid rather than alkaline.

The precipitate of barium chromate is allowed to settle for an hour and filtered off on a small filter and washed with water containing ammonium chromate until free of soluble strontium and calcium (test—addition of NH_4OH and $(NH_4)_2CO_3$ produces no cloudiness), and then with water until practically free of ammonium chromate (e.g., only slight reddish brown color with silver nitrate solution).

To separate any occluded precipitate of strontium or calcium the filter paper is pierced and the precipitate rinsed into a beaker with warm dilute nitric acid (sp.gr. 1.20) (2 cc. usually are sufficient). The solution is diluted to about 200 cc. and boiled. About 5 cc. of ammonium acetate, or enough to neutralize the free HNO_3, are added to the hot solution and then sufficient ammonium chromate to neutralize the free acetic acid, 10 cc. usually sufficient. The washing, as above indicated, is repeated. Barium is completely precipitated and may be determined either as a chromate or a sulphate or by a volumetric procedure. Strontium and calcium are in the filtrates and may be separated as follows:

(b) Separation of Strontium from Calcium. The method depends upon the insolubility of strontium nitrate and the solubility of calcium nitrate in a mixture of ether-alcohol, 1 : 1.

Solubility of $SrNO_3 = 1$ part $SrNO_3$ in 60,000 parts of the mixture. Ca easily soluble.

If the solution is a filtrate from barium, 1 cc. of nitric acid is added and the solution heated and made alkaline with ammonium hydroxide followed immediately with ammonium carbonate, the carbonates of strontium (together with some $SrCrO_4$) and calcium will precipitate. The precipitate is dissolved in hydrochloric acid and reprecipitated from a hot solution with ammonium hydroxide and ammonium carbonate. The precipitate, $SrCO_3$ and $CaCO_3$, is washed once with hot water and is then dissolved in the least amount of nitric acid, washed into a small casserole, evaporated to dryness and heated for an hour at 140 to 160° C. in an oven, or at 110° C. over night. The dry mass is pulverized and mixed with 10 cc. of ether-alcohol (absolute alcohol, one part, ether-anhydrous, one part). Several extractions are thus made, the extracts being decanted off into a flask. The residue is again dried in an oven at 140 to 160° C., then pulverized and washed into the flask with the ether-alcohol mixture and digested for several hours with frequent shaking of the flask. The residue is washed onto a filter moistened with ether-alcohol mixture. Strontium nitrate, $Sr(NO_3)_2$, remains insoluble, and may be dissolved in water and determined gravimetrically as a sulphate, oxide, or carbonate or volumetrically. Calcium is in the filtrate and may be determined gravimetrically as an oxide or volumetrically.

Instead of using a mixture of ether-alcohol, amyl alcohol may be used (hood), the mixture being kept at boiling temperature to dehydrate the alcohol to prevent solution of strontium (*b.p.* = 130° C.).

2. Separation of Barium and Strontium from Calcium.[1] The procedure depends upon the insolubility of barium nitrate, $(BaNO_3)_2$, and strontium nitrate, $Sr(NO_3)_2$, in a mixture of anhydrous ether and absolute alcohol or anhydrous amyl alcohol, whereas $Ca(NO_3)_2$ dissolves.

The mixed oxides or carbonates are dissolved in nitric acid and taken to dryness in a beaker or Erlenmeyer flask, and heated for an hour or more in an

[1] Method of Fresenius, Z. anal. Chem., **29**, 427 (1890).

oven at 140 to 160° C. Upon cooling, the mixture is treated with ten times its weight of ether-alcohol mixture and digested, cold, in the covered beaker or corked flask for about two hours with frequent stirring. An equal volume of ether is now added and the digestion continued for several hours longer. The residue is washed by decantation with ether and alcohol mixture until calcium is removed (test—no residue on platinum foil with drop of filtrate evaporated to dryness). If calcium is present in amount above 0.5 gram, the residue is dissolved in a little water, again evaporated and dried and then extracted with ether-alcohol as directed above.

Calcium is in the filtrate and may be determined by precipitation as a sulphate in the alcohol solution or as an oxide by evaporation of the ether-alcohol and precipitation as calcium oxalate, CaC_2O_4, according to directions given in the determination of calcium.

Barium and strontium may be separated by precipitation of barium as a chromate, the nitrate residue being dissolved in water and barium precipitated according to directions given under Procedure No. 1.

Amyl alcohol may be used in place of ether-alcohol by digesting the nitrates in a boiling solution (130° C.), calcium going into solution and barium and strontium remaining insoluble as nitrates.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF BARIUM

For reasons given under "Preliminary Considerations," it is advisable to take a special sample for the determination of barium that has not undergone treatment with hydrogen sulphide or ammonium hydroxide, since these may cause the loss of barium as stated.

Preparation of the Sample. The following general schemes will meet practically all conditions:

Barium in Insoluble Residue. In the complete analysis of ores the residue remaining insoluble in acids is composed largely of silica, together with difficultly soluble substances, among which is barium sulphate. This residue is best fused in a platinum dish with sodium carbonate or a mixture of sodium and potassium carbonates (long fusion is not necessary). The cooled mass is digested with hot water to remove the soluble sodium compounds, among which is silica. Barium, together with the heavy metals, remains insoluble as carbonate and may be filtered off. The residue is now treated with dilute ammonia water to remove the adhering sulphates (testing the filtrate with hydrochloric acid and barium chloride solution; the washing being complete when no white precipitate of barium sulphate forms). The carbonates are washed off the filter into a 500-cc. beaker, the clinging carbonate being dissolved by pouring a few cc. of dilute, 1 : 1, hydrochloric acid on the paper placed in the funnel. This extract is added to the precipitate in the beaker and the latter covered to prevent loss by spattering. Additional hydrochloric acid is cautiously added so that the precipitate completely dissolves and the solution contains about 10 cc. of free hydrochloric acid (sp.gr. 1.2). Barium is precipitated from this solution best as a sulphate according to directions given later.

Silicates. One gram of the finely pulverized sample is treated with 10

cc. of dilute sulphuric acid, 1 : 4, and 5 cc. of strong hydrofluoric acid. The mixture, evaporated to small bulk on the steam bath, is taken to SO_3 fumes on the hot plate. Additional sulphuric acid and hydrofluoric acid are used if required. By this treatment the silica is expelled and barium, together with other insoluble sulphates, will remain upon the filter when the residue is treated with water and filtered. Lead sulphate, if present, may be removed by washing the residue with a solution of ammonium chloride. Barium sulphate may be purified by fusion with potassium carbonate as above directed or by dissolving in hot concentrated sulphuric acid, and precipitating again as $BaSO_4$ by dilution.

Ores may be decomposed by either of the above methods or a combination of the two. Sulphide ores require roasting to oxidize the sulphide to sulphate.

Determination of Barium as a Chromate

A preliminary spectroscopic test has indicated whether a separation from calcium and strontium is necessary. If these are present, barium is separated along with strontium from calcium as the nitrate in presence of alcohol-ether mixture, according to directions given under "Separations." Barium is now precipitated as the chromate, $BaCrO_4$, from a neutral or slightly acetic acid solution, strontium remaining in solution.

Precipitation of Barium Chromate. If barium is present in the form of nitrate, together with strontium, the mixed nitrates are evaporated to dryness and then taken up with water. About 10 cc. ammonium acetate (300 grams $NH_4C_2H_3O_2$ neutralized with NH_4OH+H_2O to make up to 1000 cc.) added and the solution heated to boiling. Five cc. of 20% ammonium bichromate are added drop by drop with constant stirring and the precipitate allowed to settle until cold. The solution is decanted off from the precipitate through a filter and washed by decantation with dilute (0.5%) solution of ammonium acetate, until the excess chromate is removed, as indicated by the filtrate passing through uncolored. If much strontium was originally present, a double precipitation is necessary, otherwise the precipitate may be filtered directly into a Gooch crucible and ignited, the following paragraph directions being omitted.

Purification from Strontium. The precipitate is dissolved from the filter by running through dilute (1 : 5) warm nitric acid, poured upon the chromate, catching the solution in the beaker in which the precipitation was made; the least amount of acid necessary to accomplish this being used and the filter washed with a little warm water. Ammonium hydroxide is now added to the solution, cautiously, until a slight permanent precipitate forms and then 10 cc. of ammonium acetate solution added with constant stirring and the mixture heated to boiling. The precipitate is allowed to settle until the solution is cold and then filtered and washed by decantation as before, a Gooch crucible being used to catch the precipitate.

Ignition. The precipitate is washed once with dilute alcohol, 1 : 10, dried at 110° C., and ignited, gently at first and then to a dull red heat until the color of the chromate is uniform. It is advisable to cover the crucible at first and then after five minutes to remove the cover.

$$BaCrO_4 \times 0.6051 = BaO. \quad BaCrO_4 \times 0.5420 = Ba.$$

NOTES. The use of sodium hydrate or acetate in place of the ammonium hydroxide and acetate is sometimes recommended, owing to the slight solubility of

$BaCrO_4$ in ammonium salts, as seen by the following table, approximate figures being given:

100,000 parts of cold water dissolves	0.38 parts $BaCrO_4$
100,000 parts of hot water dissolves	4.35 parts $BaCrO_4$
100,000 of 0.5% solution of NH_4Cl dissolves	4.35 parts $BaCrO_4$
100,000 of 0.5% solution of NH_4NO_3 dissolves	2.22 parts $BaCrO_4$
100,000 of 0.75% solution of $NH_4C_2H_3O_2$ dissolves	2.00 parts $BaCrO_4$
100,000 of 1.5% solution of $NH_4C_2H_3O_2$ dissolves	4.12 parts $BaCrO_4$
100,000 of 1% acetic acid dissolves	20.73 parts $BaCrO_4$

Although the solvent action of ammonium salts is practically negligible under conditions of analysis given above, the solvent action of free acetic acid is of importance, so that it is necessary to neutralize or eliminate free mineral acids before addition of the acetate salt.

The edges of the $BaCrO_4$ precipitate upon drying may appear green, owing to the action of alcohol; upon ignition, however, the yellow chromate is obtained. The color orange yellow, when hot, fades to a light canary yellow upon cooling.

$BaCrO_4$, *mol.wt.*, 253.47; *sp.gr.*, $4.498^{15°}$; 100 cc. H_2O sol. cold will dissolve $0.00038^{18°}$ gram, hot dissolves 0.0043 gram; soluble in HCl, HNO_3, yellow rhombic plates.

Determination of Barium by Precipitation as Sulphate, $BaSO_4$

This method depends upon the insolubility of barium sulphate in water and in very dilute hydrochloric acid or sulphuric acid, one gram of the salt requiring about 344,000 cc. of hot water to effect solution.

Reaction, $BaCl_2+H_2SO_4=BaSO_4+2HCl$.

$BaSO_4$, *mol.wt.*, 233,44; *sp.gr.*, 4.47 *and* 4.33; *m.p.*, 1580° (*amorphous decomposes*); H_2O *dissolves* 0.000172° *gram and* $0.0003^{24°}$ *per* 100 *cc.* 3% HCl *dissolves* 0.0036 *gram. Soluble in conc.* H_2SO_4. *White, rhombic and amorphous forms.*

Procedure. The slightly hydrochloric acid solution of barium chloride, prepared according to directions given, is heated to boiling (volume about 200-300 cc.) and a slight excess of dilute hot sulphuric acid added. The precipitate is settled on the water bath and the clear solution then decanted through a weighed Gooch crucible or through an ashless filter paper (S. and S. 590 quality). The precipitate is transferred to the Gooch (or paper), and washed twice with very dilute sulphuric acid solution (0.5% H_2SO_4), and finally with hot water until free of acid. The precipitate is dried and ignited, at first gently and then over a good flame to a cherry red heat, for half an hour. The residue is weighed as barium sulphate, $BaSO_4$.

$$BaSO_4 \times 0.5884 = Ba, \text{ or } \times 0.6569 = BaO, \text{ or } \times 0.8455 = BaCO_3.$$

NOTES. The determination of barium is the reciprocal of the determination of sulphur or sulphuric acid. Precautions and directions given for the sulphur precipitation apply here also, with the exception that dilute sulphuric acid is used as the precipitating reagent in place of barium chloride.

The author found that precipitation of barium sulphate in a large volume of cold solution containing 10 cc. of concentrated hydrochloric acid per 1600 cc. of solution, by adding a slight excess of cold dilute sulphuric acid in a fine stream, exactly in the manner that barium chloride solution is added in the precipitation of sulphur, and allowing the precipitate to settle, at room temperature, for several hours (preferably over night), gives a precipitate that is pure and does not pass through the Gooch asbestos mat. We refer to the chapter on Sulphur for directions for filtering, washing, and ignition of the residue.

VOLUMETRIC METHODS FOR THE DETERMINATION OF BARIUM

Titration of the Barium Salt with Dichromate

This method is of value for an approximation of the amount of barium present in a solution that may also contain calcium, strontium, and magnesium or the alkalies. It depends upon the reaction

$$2BaCl_2+K_2Cr_2O_7+H_2O=2BaCrO_4+2KCl+2HCl.$$

N/10 $K_2Cr_2O_7$ (precipitation purposes) contains 7.355 grams pure salt per liter.

Procedure. The solution containing the barium is treated with ammonia until it just smells of it. (If an excess of ammonia is present the solution is made faintly acid with acetic acid.) It is then heated to about 70° C. and the standard dichromate added, with stirring until all the barium is precipitated and the clear supernatant solution is a faint yellow color from the slight excess of the reagent. For accurate work it is advisable to titrate the precipitate formed by one of the methods given below. One cc. $K_2Cr_2O_7=0.00687$ gram Ba. (Note reaction given above.)

NOTE. An excess of potassium dichromate may be added, the precipitate filtered off, washed and the excess of dichromate determined as stated below.

Reduction of the Chromate with Ferrous Salt and Titration with Permanganate

Ferrous sulphate reacts with barium chromate as follows:

$$2BaCrO_4+6FeSO_4+8H_2SO_4=3Fe_2(SO_4)_3+Cr_2(SO_4)_3+2BaSO_4+8H_2O.$$

An excess of ferrous salt solution is added and the excess determined by titration with N/10 $KMnO_4$ solution. $Fe=\frac{1}{2}Ba$.

Reagents. N/10 solution of $KMnO_4$. N/10 $FeSO_4$ (27.81 grams per liter) or $FeSO_4\cdot(NH_4)_2SO_4$ (39.226 grams per liter). One cc. =0.004579 Ba.

Procedure. The well-washed precipitate of barium chromate is dissolved in an excess of standard N/10 ferrous ammonium sulphate solution containing free sulphuric acid. The excess ferrous salt is titrated with standard N/10 potassium permanganate solution.

(Cc. N/10 ferrous solution minus cc. permanganate titration) multiplied by 0.004579 gives grams barium in the solution. Iron factor to barium is 0.8187.

Potassium Iodide Method

The procedure depends upon the reactions:

1. $2BaCrO_4+6KI+16HCl=2BaCl_2+2CrCl_3+6KCl+8H_2O+6I.$
2. $3I_2+6Na_2S_2O_3=6NaI+3Na_2S_4O_6.$

Procedure. The precipitate, $BaCrO_4$, is dissolved in 50 to 100 cc. of dilute hydrochloric acid and about 2 grams of solid potassium iodide salt added and allowed to react about ten minutes. The liberated iodine is now titrated

with N/10 thiosulphate. Near the end of the titration starch solution is added and followed by N/10 thiosulphate until the color disappears.

One cc. N/10 $Na_2S_2O_3$ = 0.004579 gram Ba.

Titration of Barium Carbonate with Standard Acid

To the well-washed barium carbonate, $BaCO_3$, an excess N/10 H_2SO_4 is added and the excess acid determined.

One cc. N/10 acid = 0.00687 gram Ba.

ANALYSIS OF BARYTES AND WITHERITE

Barytes or heavy spar is a variety of native barium sulphate, and witherite a native barium carbonate. These minerals are typical examples of barium-bearing ores. The analysis may involve the determination of barium and calcium sulphates or carbonates, magnesia, iron and aluminum oxides and moisture. Traces of lead, copper, and zinc may be present, as well as sulphide, sulphur and fluorine in fluorspar. The following is an approximate composition of a high-grade sample:

$BaSO_4$ = 96%, $CaCO_3$ = 1.5%, $MgCO_3$ = 0.3%, SiO_2 = 0.5%, Al_2O_3 = 0.5%, Fe_2O_3 = 0.2%, H_2O = 0.5%.

For complete analysis treat as directed under preparation of the sample.

Procedure for Commercial Valuation of the Ore

Barium Sulphate and Silica

One gram of the finely pulverized sample is digested with about 50 cc. of concentrated hydrochloric acid and taken to dryness on the steam bath. The residue is taken up with 50 cc. of water, 10 cc. of hydrochloric acid added, and the mixture heated on the steam bath for ten minutes, then heated to boiling and filtered. The residue of barium sulphate and silica is washed well with hot water containing a little hydrochloric acid and finally with pure water. It is now ignited and weighed as $BaSO_4 + SiO_2$, or total insoluble matter.

The residue in a platinum dish is now treated with a little hydrofluoric acid + sulphuric acid, and silica expelled as usual. The residue ignited = $BaSO_4$.

Silica = difference between total insoluble matter and $BaSO_4$.

Barium Carbonate

Barium, originally present as a carbonate, will be found in the filtrate together with iron, alumina, etc., and may be precipitated by addition of sulphuric acid. Barium sulphate is filtered off, washed, ignited, and weighed. $BaSO_4 \times 0.84555 = BaCO_3$.

Iron and Alumina Oxides

These are determined in the filtrate from barium precipitation in the usual way.

Calcium and Magnesium

Determined in the filtrate from iron and alumina by the regular procedures.

Soluble Sulphates

One gram of the powdered sample is boiled with 20 cc. conc. HCl and 200 cc. water, the insoluble residue filtered off and washed. The filtrate contains the soluble sulphate. This may be precipitated by addition of $BaCl_2$ solution according to the procedure for sulphur. $BaSO_4 \times 0.5833 = CaSO_4$. $BaSO_4 \times 0.2402 = CaO$.

If lime, CaO, thus calculated, is less than lime precipitated as oxalate, the difference is calculated to $CaCO_3$ if CO_2 is present, otherwise to CaO.

Loss on Ignition

Represents water free and combined, carbon dioxide and organic matter.

BISMUTH

WILFRED W. SCOTT

Bi, *at.wt.* 208.0; *sp.gr.* 9.7474; *m.p.* 271°;[1] *b.p.* 1420° C.; *oxides*, Bi_2O_3, Bi_2O_5.

DETECTION

Bismuth is precipitated from its solution, containing free acid, by H_2S gas, as a brown sulphide, Bi_2S_3. The compound is insoluble in ammonium sulphide (separation from arsenic, antimony, and tin), but dissolves in hot dilute nitric acid (separation from mercury). The nitrate, treated with sulphuric acid and taken to SO_3 fumes, is converted to the sulphate and dissolves upon dilution with water (lead remains insoluble as $PbSO_4$). Bismuth is precipitated from this solution by addition of ammonium hydroxide, white $Bi(OH)_3$ being formed (copper and cadmium dissolve). If this hydroxide is dissolved with hydrochloric acid and then diluted with a large volume of water, the white, basic salt of bismuth oxychloride, BiOCl, is precipitated. The compound dissolves if sufficient hydrochloric acid is present. It is insoluble in tartaric acid (distinction from antimony).

Reducing Agents. Formaldehyde in alkaline solution, hypophosphorous acid, potassium or sodium stannite, reduce bismuth compounds to the metallic state. For example, a hot solution of sodium stannite poured onto the white precipitate of $Bi(OH)_3$ on the filter will give a black stain. The test is very delicate and enables the detection of small amounts of the compound.

$$3K_2SnO_2+2BiCl_3+6KOH=2Bi+3K_2SnO_3+6KCl+3H_2O.$$

Blowpipe Test. A compound of bismuth heated on charcoal with a powdered mixture of carbon, potassium iodide and sulphur, will give a scarlet incrustation on the charcoal.

ESTIMATION

The determination of bismuth is required in complete analysis of ores of cobalt, nickel, copper, silver, lead, and tin, in which it is generally found in small quantities. In evaluation of bismuthite, bismuth ochre, etc. In the analysis of the minerals wolfram, molybdenite. It is determined in the residues from the refining of lead (the principal source of bismuth in the United States). In the analysis of alloys—antifriction metals, electric fuses, solders, stereotype metals, certain amalgams used for silvering mirrors (with or without lead or tin), and in bismuth compounds.

Preparation and Solution of the Sample

In dissolving the substance, the following facts must be kept in mind: nitric acid is the best solvent of the metal. Although it is soluble in hot sulphuric acid, it is only very slightly soluble in the cold acid. The metal is practically insoluble in hydrochloric acid, but readily dissolves in nitrohydrochloric acid.

[1] U. S. Bureau of Standards Cir. 35.

The hydroxides, oxides, and most of the bismuth salts are readily soluble in hydrochloric, nitric, and sulphuric acids.

Ores or Cinders. One gram of the finely pulverized ore or cinder (or larger amounts where the bismuth content is very low) is treated in a 400-cc. beaker with 5 cc. of bromine solution ($Br+KBr+H_2O$),[1] followed by the cautious addition of about 15 cc. of HNO_3 (sp.gr. 1.42). When the violent action has ceased, which is apt to occur in sulphide ores, the mixture is taken to dryness on the steam bath, 10 cc. of strong HCl and 20 cc. of concentrated H_2SO_4 and the covered sample heated until SO_3 fumes are freely evolved. The cooled solution is diluted with 50 cc. of water and gently heated until only a white or light gray residue remains. The solution is filtered and the residue washed with dilute H_2SO_4 (1 : 10), to remove any adhering bismuth. Silica, the greater part of the lead (also $BaSO_4$) remain in the residue, whereas the bismuth, together with iron, alumina, copper, antimony, etc., are in the solution. Details of further treatment of the solution to effect a separation of bismuth are given under "Separations" and the procedures for determination of bismuth.

Alloys, Bearing Metal, etc. One gram of the borings, placed in a 400-cc. beaker, is dissolved by adding 20 cc. of concentrated HCl and 5 cc. of strong HNO_3. The alloy will usually dissolve in the cold, unless considerable lead is present, in which case prolonged heating on the steam bath may be necessary. (A yellow or greenish-yellow color at this stage indicates the presence of copper.) Lead may now be removed either as a sulphate by taking to SO_3 fumes with H_2SO_4 or by precipitating as a chloride, in the presence of alcohol, according to directions given under Separations. The bismuth is determined in the filtrate from lead according to one of the procedures given under the quantitative methods.

Lead Bullion, Refined Lead.[2] Ten to twenty-five grams of the lead, hammered or rolled out into thin sheets and cut into small pieces, are taken for analysis. The sample is dissolved by a mixture of 250 cc. of water and 40 cc. of strong nitric acid, in a large covered beaker, by warming gently, preferably on the steam bath. When the lead has dissolved, the beaker is removed from the heat and dilute ammonia (1 : 2) added to the warm solution, very cautiously and finally drop by drop until the free acid is neutralized and the liquid remains faintly opalescent, but with no visible precipitate. Now 1 cc. of dilute HCl (1 : 3) is added. The solution will clear for an instant and then a crystalline precipitate of bismuth oxychloride will form, if any considerable amount of bismuth is present. The beaker is now placed on the steam bath for an hour, during which time the bismuth oxychloride will separate out, together with a small amount of lead and with antimony if present in appreciable amounts. The further isolation and purification of bismuth is given under "Separations." In brief—antimony is removed by dissolving the precipitate in a small amount of hot dilute HCl (1 : 3), precipitating bismuth, traces of lead, and the antimony by H_2S, dissolving out the antimony sulphide with warm ammonium sulphide, dissolving the Bi_2S_3 and PbS in HNO_3 and reprecipitation of the bismuth according to the procedure given above. Bismuth is now determined as the oxychloride. Further details of this method are given under the gravimetric procedures for bismuth.

[1] Bromine solution is made by dissolving in water 75 grams of KBr, to which are added 50 grams of liquid bromine and the mixture diluted to 500 cc. with water.

[2] Bismuth in Refined Lead. "Technical Methods of Ore Analysis." A. H. Low.

SEPARATIONS

The following procedures are given in the order that would be followed in the complete analysis of an ore, in which all the constituents are sought. This general scheme, however, is not required for the majority of bismuth-bearing samples commonly met with in the commercial laboratory, direct precipitations of bismuth frequently being possible.

Separation of Bismuth from Members of Subsequent Groups, Fe, Cr, Al, Mn, Co, Ni, Zn, Mg, the Alkaline Earths and Alkalies, together with Rare Elements of these Groups. The solution should contain 5 to 7 cc. of concentrated hydrochloric acid (sp.gr. 1.19) for every 100 cc. of the sample. The elements of the hydrogen sulphide group are precipitated by saturating the solution with H_2S (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo, Se, Te, Au, Pt). The members of subsequent groups remain in solution and pass into the filtrate.

Separation of Bismuth from Arsenic, Antimony, Tin, Molybdenum, Tellurium, Selenium. In presence of mercury, the soluble members of the hydrogen sulphide group are separated from the insoluble sulphides by digesting the precipitate above obtained with ammonium sulphide; in absence of mercury, however, which is generally the case, digestion of the sulphides with sodium hydroxide and sodium sulphide solution is preferred, the general procedure being followed. Mercury, lead, bismuth, copper, and cadmium remain in the residue, whereas the other members of the group dissolve.

Separation of Bismuth from Mercury. The insoluble sulphides, remaining from the above treatment with ammonium sulphide after being washed free of the soluble members of this group, are placed in a porcelain dish and boiled with dilute nitric acid (sp.gr. 1.2 to 1.3). The solution thus obtained is filtered, upon dilution, from the insoluble sulphide of mercury. A little of the lead may remain as $PbSO_4$, the solution may contain lead, bismuth, copper, and cadmium.

Separation of Bismuth from Lead. This is the most important procedure in the determination of bismuth as the separation is almost invariably necessary, as these elements commonly occur together. Bismuth produced in the United States in 1912 was obtained entirely from the residues in the refining of lead.[1]

There are two general procedures for the separation of lead and bismuth.

A. Precipitation of lead either as lead sulphate or as lead chloride, the bismuth remaining in solution under the conditions of the precipitation.

B. Precipitation of bismuth as the oxychloride or subnitrate, lead remaining in solution.

Precipitating Lead as $PbSO_4$. This procedure is generally used in the process of a complete analysis of an ore containing lead and bismuth. The nitric acid solution of the sulphides, obtained upon removal of the soluble group and mercury by boiling the insoluble sulphides with dilute nitric acid, is treated with about 10 cc. of strong sulphuric acid, and taken to SO_3 fumes by heating. The cooled sulphate solution is diluted with water and the insoluble lead sulphate filtered off and washed with dilute sulphuric acid solution (1 : 20). Bismuth passes into solution, together with copper and cadmium, if also present in the original sample.

[1] Mineral Industry, 1912, p. 98.

Precipitation of Lead as $PbCl_2$. This separation is used in the complete analysis of pig lead, the details of the separation being given under this subject.

As the separation of bismuth from lead by precipitation of the former element as the oxychloride or subnitrate is incorporated in the quantitative methods following, it will not be taken up here.

Separation of Bismuth from Copper and Cadmium. This separation is accomplished by precipitating bismuth as the oxychloride with hydrochloric acid, or as the carbonate by adding an excess of ammonium carbonate to the solution nearly neutralized by ammonia, or as the hydroxide by adding an excess of ammonia. Details of these procedures are given under the gravimetric methods for determining bismuth.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF BISMUTH

Determining Bismuth by Precipitation and Weighing as the Basic Chloride, BiOCl

The determination depends upon the formation of the insoluble oxychloride, BiOCl, when a hydrochloric acid solution of bismuth is sufficiently diluted with water, the following reaction taking place, $BiCl_3 + H_2O = BiOCl + 2HCl$.

The procedure is recommended for the determination of bismuth in refined lead, bearing metal, and bismuth alloys. Copper, cadmium, and lead do not interfere; appreciable amounts of antimony and tin, however, should be removed by H_2S precipitation and subsequent treatment with Na_2S, and the residual sulphides dissolved in hot dilute nitric acid, according to directions given under "Separations."

Properties of BiOCl. *Mol.wt.*, 259.46; *sp.gr.*, $7.717^{15°}$; *m.p.*, red heat; *insol. in* H_2O *and in* $H_2C_4H_4O_6$, *soluble in acids. Appearance is white, quadratic crystalline form.*

Procedure. The solution of bismuth, freed from appreciable amounts of tin and antimony, is warmed gently and treated with sufficient ammonia to neutralize the greater part of the free acid. At this stage a precipitate is formed by the addition, which dissolves with difficulty; the last portion of the dilute ammonia (1 : 2) is added drop by drop, the solution is diluted to about 300 cc., and the remainder of the free acid neutralized with dilute ammonia added cautiously until a faint opalescence appears, but not enough to form an appreciable precipitate. One to 3 cc. of dilute hydrochloric acid (1 part HCl sp.gr. 1.19 to 3 parts H_2O) are now added, the mixture stirred and the bismuth oxychloride allowed to settle for an hour or so on the steam bath, then filtered hot by decanting off the clear solution through a weighed Gooch crucible. The precipitate is washed by decantation twice with hot water and finally washed into the Gooch, then dried at 100° C. and weighed as BiOCl.

$$BiOCl \times 0.8017 = Bi.$$

NOTE. Three cc. of dilute hydrochloric acid (or 1 cc. conc. HCl, sp.gr. 1.19) are sufficient to completely precipitate 1 gram of bismuth from solution.

Determination of Bismuth as the Oxide, Bi_2O_3

Preliminary Considerations. The determination of bismuth as the oxide requires the absence of hydrochloric acid or sulphuric acid from the solution of the element, since either of these acids invariably contaminates the final product. In presence of these acids, which is frequently the case, determination of bismuth by precipitation as Bi_2S_3 or by reduction to the metal and so weighing is generally recommended; a brief outline of the methods is given later; a solution of bismuth free from hydrochloric acid and practically free of sulphuric acid may be obtained by precipitating Bi_2S_3, together with CuS, CdS, and PbS, the amount of sulphuric acid formed by the reaction being negligible. Bismuth should be in a nitric acid solution, free from antimony and tin.

Two general conditions will be considered: 1. Solutions containing lead. Copper and cadmium may also be present. 2. Solutions free from lead. Copper and cadmium may be present.

1. Separation from Lead, Copper, and Cadmium, by Precipitation as Basic Nitrate.[1] Neither the sulphuric or hydrochloric acid methods may be employed for effecting the separation of lead by precipitation. Fortunately advantage may be taken of the fact that bismuth nitrate is changed by the action of water into an insoluble basic salt, while lead, copper and cadmium do not undergo such a transformation.

Procedure. The bismuth nitrate solution is evaporated to syrupy consistency and hot water added with constant stirring with a glass rod. The solution is again evaporated to dryness, and the hot-water treatment repeated. Four such evaporations are generally sufficient to convert the bismuth nitrate completely into the basic salt; when this stage is reached the addition of water will fail to produce a turbidity. The solution is finally evaporated to dryness and, when free from nitric acid, is extracted with cold ammonium nitrate solution (1.NH_4NO_3 : 500 H_2O) to dissolve out the lead and other impurities. After allowing to stand some time with frequent stirring, the solution is filtered and the residue washed with ammonium nitrate solution, then dried.

Ignition to Bismuth Oxide. As much of the precipitate as possible is transferred to a weighed porcelain crucible, the filter is burned and the ash added to the main precipitate. This is now gently ignited over a Bunsen burner. Too high heating will cause the oxide to fuse and attack the glaze of the crucible.

Properties. $Bi(OH)_2NO_3$ *mol.wt.*, 304.03; *sp.gr.*, 4.928[15°]; *decomp.*, 260°; *insol. in* H_2O; *sol. in acids; hexagonal plates.*

Bi_2O_3 = *mol. wt.*, 464.0; *sp.gr.*, 8.8 *to* 9.0; *m.p.*, 820 to 860°; *insoluble in cold water and in alkalies, but soluble in acids; yellow tetragonal crystals.*

$$Bi_2O_3 \times 0.8965 = Bi.$$

2. Precipitation of Bismuth as the Subcarbonate or Hydroxide, Lead being Absent. Either of these procedures effects a separation of bismuth from copper and cadmium.

A. Procedure. Precipitation of the Subcarbonate. The solution is diluted to about 300 cc. and dilute ammonia added cautiously until a faint turbidity is obtained and then an excess of ammonium carbonate. The solution

[1] J. Löwe, Jour. prak. Chem., (1), 74, 344, 1858.

is heated to boiling, the precipitate filtered off, washed with hot water, dried and ignited according to directions given in the bismuth subnitrate method. The residue is weighed as Bi_2O_3.

B. Procedure. Isolation of Bismuth by Precipitation as the Hydroxide.[1] The solution is taken to dryness and the residue treated with 5 cc. of nitric acid (1 : 4) and 25 cc. of water added. The resulting solution is poured, with constant stirring, into 25 cc. of concentrated ammonia and 50 cc. of 4% hydrogen peroxide. Upon settling of the bismuth hydroxide, the clear solution is filtered off and the residue is treated with more ammonia and peroxide. It is then filtered onto a filter paper, washed with hot, dilute ammonium hydroxide, (1 : 8), followed by hot water and washed free of any adhering copper or cadmium (no residue when a drop is evaporated on platinum foil). Re-solution in hot dilute nitric acid and reprecipitation may sometimes be necessary to obtain the pure product. The hydroxide may be dried, ignited and weighed as Bi_2O_3 according to directions already given on page 66.

Properties. $Bi_2O_3 \cdot CO_2 \cdot H_2O$, *mol.wt.*, 526.02; *sp.gr.*, 6.86; *decomp. by heat; insoluble in water, soluble in acids, insoluble in* Na_2CO_3; *white precipitate.*

$Bi(OH)_3$, *mol.wt.*, 259.02; *loses* $1\frac{1}{2}$ H_2O *at* 150°; *insol. in cold water and in alkalies; soluble in acids; white precipitate.*

Determination of Bismuth as the Sulphide, Bi_2S_3

The procedure is applicable to the determination of bismuth in a hydrochloric or sulphuric acid solution, freed from other members of this group.

Procedure. Bismuth sulphide is precipitated by passing H_2S into the slightly acid solution, preferably under pressure. When the precipitation is complete, the bismuth sulphide, Bi_2S_3, is filtered off into a weighed Gooch crucible, the precipitate washed with H_2S water, then with alcohol to remove the water, followed by carbon disulphide to dissolve out the precipitated sulphur, then alcohol to remove the disulphide, and finally with ether. After drying for fifteen to twenty minutes, the residue is weighed as Bi_2S_3. This weight multiplied by 0.8122 = Bi.

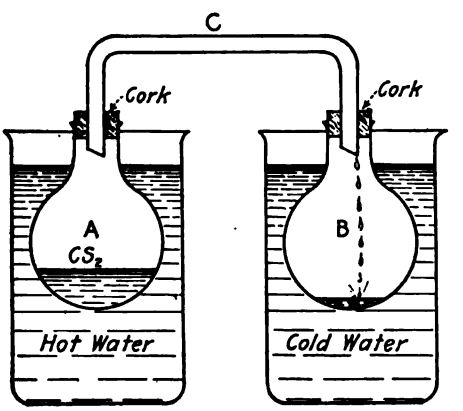

FIG. 7.—Purification of Carbon Disulphide.

NOTE. The carbon disulphide used should be freshly distilled. This may be accomplished by placing the carbon disulphide in a small flask (*A*, Fig. 7) connected by means of a glass tube (*C*) to a second flask (*B*), cork stoppers being used. The vessels are immersed in beakers of water, the container with the reagent being placed in hot water (60–80° C.) and the empty flask in cold water. The reagent quickly distills into the empty flask in pure form.

Properties of Bismuth Sulphide. Bi_2S_3, *mol.wt.*, 512.21; *sp.gr.*, 7–7.81; *decomposed by heat, solubility* = 0.000018g. *per* 100 cc. *cold* H_2O; *soluble in nitric acid; brown rhombic crystals.*

[1] P. Jannasch, Zeit. anorg. Chem., 8, 302, 1895.

Determination of Bismuth as the Metal

Reduction with Potassium Cyanide.[1] Bismuth precipitated as the carbonate and ignited to the oxide according to the procedure given, is fused in a weighed porcelain crucible with 5 times its weight of potassium cyanide over a low flame. The cooled melt is extracted with water, pouring the extracts through a filter that has been dried and weighed with the crucible. Bismuth is left undissolved as metallic bismuth. After washing with water, alcohol, and ether, the filter, with the metal and loosened pieces of porcelain glaze, is dried at 100° C. together with the crucible. These are then weighed and the increased weight taken as the amount of bismuth present in the sample.

Electrolytic Deposition of Bismuth

With samples containing less than 0.03 gram bismuth, the metal may be satisfactorily deposited by electrolysis of its sulphuric acid solution, lead having been removed previously by sulphuric acid by the standard procedure. The solution contains about 6 cc. of strong sulphuric acid per 100 cc. This is electrolyzed with a current of 0.6 to 0.7 ampere and about 2.7 to 3 volts Further details of this method may be found in "Technical Methods of Ore Analysis," by A. H. Low, page 54, VII Edition. John Wiley & Sons.

VOLUMETRIC DETERMINATION OF BISMUTH

Determination of Bismuth by Precipitation as Oxalate and Titration by Potassium Permanganate[2]

Normal bismuth oxalate, produced by addition of oxalic acid to a nitric acid solution of the element, boiled with successive portions of water, is transformed to the basic oxalate. This may be titrated with potassium permanganate in presence of sulphuric acid.

Procedure. ***Preparation of the Sample.*** One gram of the finely ground sample is treated with 5 to 10 cc. of concentrated nitric acid and digested on the steam bath and finally evaporated to dryness, the residue is taken up with 5 cc. of nitric acid (sp.gr. 1.42)+25 cc. of water, and diluted to 100 cc.

Precipitation of the Oxalate. About 5 grams of ammonium oxalate or oxalic acid are added and the liquid boiled for about five minutes, the precipitate allowed to settle and the supernatant solution filtered off. The precipitate is boiled twice with 50-cc. portions of water and the washings poured through the same filter. If the filtrate still passes through acid, the washing is continued until the acid is removed and the washing passing through the filter is neutral. The bulk of the basic oxalate precipitate is placed in a beaker and that remaining on the filter paper is dissolved by adding 2 to 5 cc. of hydrochloric acid, 1 : 1, the solution being added to the bulk of the precipitate.

[1] Method by H. Rose, Pogg. Ann., **110**, p. 425.
Vanino and Treubert (Ber., **31** (1898), 1303), reduce bismuth by adding formaldehyde to its slightly acid solution and then making strongly alkaline with 10% NaOH solution and warming. N.B. Treadwell and Hall, Anal. Chem., p. 181, 3d Ed.

[2] The method is rapid and is sufficiently accurate for commercial work. Warwick and Kyle (C. N., **75**, 3).
Muir and Robbs, J. C. S., **41**, 1.

This is now warmed until it goes into solution and the liquid is diluted to 250 cc. with hot water. Dilute ammonia is now added until the free acid is neutralized; the resulting precipitate is taken up with dilute sulphuric acid, 1 : 4, added in slight excess. The resulting solution, warmed to 70°, is titrated with standard potassium permanganate.

One cc. $KMnO_4$ N/10 = 0.0104 gram Bi.

NOTE. Lead, copper, arsenic, iron, zinc, and tellurium do not interfere. Hydrochloric acid should not be used to dissolve the sample, as it interferes with the oxalate precipitation.

Cinchonine Potassium Iodide, Colorimetric Method [1]

This method is applicable for the determination of small amounts of bismuth, 0.00003 to 0.00015 gram, in ores and alloys. The procedure depends upon the fact that bismuth nitrate produces a crimson or orange color when its solution is added to a solution of cinchonine potassium iodide, the intensity of the color depending upon the amount of bismuth in the resulting product.

Special Reagents. ***Cinchonine Potassium Iodide Solution.*** Ten grams of cinchonine are dissolved by treating with the least amount of nitric acid that is necessary to form a viscous mass and taking up with about 100 cc. of water. The acid is added a drop at a time, as an excess must be avoided. Twenty grams of potassium iodide are dissolved separately and cinchonine solution added. The resulting mixture is diluted with water to 1000 cc. After allowing the reagent to stand forty-eight hours, any precipitate formed is filtered off and the clear product is ready for use. The reagent preserved in a glass-stoppered bottle keeps indefinitely. It should be filtered free of suspended matter before use.

Standard Bismuth Solution. One gram of metallic bismuth is dissolved in the least amount of dilute nitric acid (1 : 1) that is necessary to keep it in solution and diluted to 1000 cc., in a graduated flask. One hundred cc. of this solution is diluted to 1000 cc. One cc. of this diluted solution contains 0.0001 gram bismuth.

Procedure. ***Isolation of Bismuth.*** The solution is freed from lead by H_2SO_4, and from arsenic, antimony, and tin by precipitation of the sulphides and extraction with Na_2S solution. The residual sulphides are dissolved in hot dilute nitric acid, according to the standard methods of procedure. The free nitric acid is nearly neutralized by the cautious addition of dilute ammonia, the last portion being added drop by drop, until a faint cloudiness is evident, and then 10 to 15 cc. of 10% ammonium carbonate are added with constant stirring. The mixture is digested for about three hours on the steam bath, the clear solution decanted through a small filter, the residue washed by decantation once or twice with hot water containing ammonium carbonate and then on the filter twice with pure hot water.

Colorimetric Comparison

The residue of bismuth basic carbonate is dissolved in the least amount of dilute nitric acid necessary to effect solution and the filter washed free of bismuth with a little water containing a few drops of nitric acid. The solution is made up to a definite volume, 50 cc. or 100 cc. according to the bulk of

[1] Method of W. C. Ferguson.

precipitate dissolved. Two small beakers placed side by side may be used for the color comparison, a sheet of white paper or tile being placed under the beakers. Two 50-cc. Nessler tubes, however, are preferred. Three cc. of cinchonine solution are added to each container. From a burette the bismuth nitrate sample is run into one of these containers in just sufficient quantity to color the reagent a crimson or orange tint. The exact volume required to do this is noted and the equivalent amount of sample used calculated. (If no color is produced bismuth is absent.) The reagent in the adjacent beaker or Nessler tube is diluted to 5 to 7 cc., and into this is run, from a burette, the standard bismuth nitrate solution until the color exactly matches the sample. From the cc. of the standard required the amount of bismuth in the sample can readily be calculated.

Reaction. $3KI+C_{19}H_{22}N_2OKI+Bi(NO_3)_3=C_{19}H_{22}N_2OKIBiI_3+3KNO_3$.

Precautions. The sensitiveness of the method is lost if the depth of color is too great. It is necessary, then, to add the sample to the cinchonine reagent in such quantity only as will produce a light crimson or orange color.

Solutions in the comparison tubes or beakers must not be overdiluted, since the bismuth salt formed by the reaction of the cinchonine reagent is soluble in water with the disappearance of color in too dilute solutions.

Comparison must be expeditiously made, as a precipitate is apt to form upon standing, and iodine will sometimes separate.

The order of addition must be observed; e.g., the bismuth solution is added to the cinchonine reagent, never the reverse.

Colorimetric Determination of Bismuth. Bismuth Iodide Method [1]

Bismuth iodide gives an intense yellow, orange, or red color to its solution. The color is not destroyed by SO_2, as is that of free iodine. The intensity of the color varies as follows:

1 part of bismuth in 10,000 parts of water produces an orange-colored solution.
1 part of bismuth in 40,000 parts of water produces a light orange color.
1 part of bismuth in 100,000 parts of water produces a faint yellow color.

Reagents. ***Standard Bismuth Solution.*** One gram of bismuth is dissolved in 3 cc. of strong nitric acid and with 2.8 cc. of water and made up to 100 cc. with glycerine. Glycerine is added to keep the BiI_3 in solution. Glycerine is not necessary for amounts of bismuth below 0.0075 gram per cc.

Potassium Iodide Solution. Five grams of potassium iodide dissolved in 5 cc. of water is diluted to 100 cc. with glycerine.

Procedure. The sample is dissolved with just sufficient nitric acid and water necessary to cause solution, 10 cc. of glycerine and 10 cc. of potassium iodide solution added and the sample diluted to 50 cc. Comparison is now made with 10 cc. of the standard bismuth solution to which has been added 10 cc. of potassium iodide and 30 cc. of water. It is advisable to have the standard stronger in bismuth than the sample and to draw out the standard from the comparison cylinder until the two colors match.

[1] T. C. Thresh, Pharm. Jour., 641, 1880.

BORON

WILFRED W. SCOTT

B, at.wt. 11.0; { *amorp. sp.gr.* 2.45; *m.p.* 2200°; *b.p. sublimes.*
cryst. sp.gr. 2.55; *m.p.* 2500°; *b.p.* 3500° C; *oxide,* B_2O_3

DETECTION

Flame Test. Boric acid is displaced from its salts by nearly all acids, including even carbonic acid. Upon ignition, however, it in turn drives out other acids which are volatile at lower temperatures. A powdered borate, previously calcined, is moistened with sulphuric acid and a portion placed on the loop of a platinum wire is heated to expel the sulphuric acid,[1] then moistened with glycerine and placed in the colorless flame; a green color will be imparted to the flame. Copper salts should be removed with H_2S and barium as $BaSO_4$ if present, as these also color the flame green.

The flame test may be conveniently made by treating the powdered sample in a test-tube with sulphuric acid and alcohol (preferably methyl alcohol). A cork carrying a glass tube is inserted and the test-tube gently warmed. The escaping gas will burn with a green flame.

The test may be made by igniting the mixture of powder, alcohol, and sulphuric acid in an open porcelain dish. The green color will be seen in presence of a borate. The test is not as delicate as the one with the test-tube.

Borax Bead. $Na_2B_4O_7 \cdot 10H_2O$ fused in a platinum loop, swells to several times its original volume as the water of crystallization is being driven out, then contracts to a clear molten bead. If the bead is dipped into a weak solution of cobalt and plunged into the flame, until it again becomes molten, the bead upon cooling will be colored blue.

Turmeric Test. A few drops of acetic acid are added together with 2 or 3 drops of an alcoholic turmeric solution to an alcoholic extract of the sample, placed in a porcelain dish. The solution is diluted with water and then evaporated to dryness on the water bath. 1/1000 milligram of boric acid will produce a distinct color, 2/100 milligram will give a strong reddish-brown colored residue, which becomes bluish-black when treated with a drop of sodium hydroxide solution.

ESTIMATION

The determination of boron is required in the valuation of borax, $Na_2B_4O_7 \cdot 10H_2O$; boracite, $4MgB_4O_7 2MgO MgCl_2$; borocalcite, $CaB_4O_7 \cdot 6H_2O$; hydroboracite; boronatrocalcite, etc., the element being reported generally as the oxide, B_2O_3. The determination is required for obtaining the true value of commercial boric acid, in the analysis of fluxes and certain pigments. It is determined as a food-preservative in milk, meat, canned goods, etc. The element is determined in certain alloys of nickel, cobalt, zinc, chromium, tungsten, molybdenum and in the analysis of steel.

[1] Silicates should be mixed with potassium fluoride and potassium acid sulphate, $KHSO_4$, then held in the flame.

Preparation and Solution of the Sample

It will be recalled that crystalline boron is scarcely attacked by acids or alkaline solutions; the amorphous form, however, is soluble in concentrated nitric and sulphuric acids. Both forms fused with potassium hydroxide are converted to potassium metaborate. Boric acid is more readily soluble in pure water than in hydrochloric, nitric, sulphuric, or acetic acids, but still more soluble in tartaric acid (Herz, Chem. Zentr., 1903, 1, 312). It is soluble in alcohol and volatile oils. Borax is insoluble in alcohol. With acids it becomes transposed to boric acid and the sodium salt of the acid.

Boric Oxide in Silicates, Enamel, etc. About 0.5 gram of the finely ground material is fused with five times its weight of sodium carbonate, the melt extracted with water and the extracts, containing the sodium salt of boric acid, evaporated to small volume. The greater part of the excess sodium carbonate is neutralized with hydrochloric acid and finally made acid with acetic acid (litmus paper test = red). Boric oxide is now determined by the distillation process according to the procedure given later in the chapter.

Boronatrocalcite, Borocalcite, Boracite, Calcium Borate. Ten grams of the powdered material is placed in a flask with a reflux condenser and about 50 cc. of normal hydrochloric acid added and the mixture boiled for half an hour. The contents of the flask, together with the washings, including those of the reflux condenser (CO_2-free water being used), are filtered into a 500-cc. flask and made to volume with CO_2-free water. Fifty cc. of this solution is titrated with half-normal sodium hydroxide, using paranitrophenol indicator. When a yellow color appears the hydrochloric acid has been neutralized. A second 50-cc. portion is now taken for analysis and the free hydrochloric acid neutralized with sodium hydroxide, using the amount of caustic required in the trial analysis (this time without an indicator). Mannitol or glycerol are now added together with phenolphthalein indicator and the boric acid determined by titration according to the procedure given under the volumetric determinations for borax and boric acid.

Borax, Boric Acid. Ten grams of the material are dissolved in about 300 cc. of water (free from CO_2) and made to 500 cc. in a graduated flask, with pure water. One hundred-cc. portions are taken for analysis and the solution titrated, in presence of mannitol or glycerol, according to directions given under the volumetric procedures.

Boric Acid in Mineral Water. Water containing more than 0.1 gram boric acid per liter, 200 to 300 cc., is evaporated to small volume, the carbonates of calcium, magnesium, etc., filtered off, the filtrate and washings concentrated, slightly acidified with acetic acid and boric acid determined by the distillation process.

With water containing traces of boric acid, 10 to 15 liters are evaporated down to about 1 liter and the deposited salts filtered off and washed with hot water. The filtrate is evaporated down to a moist residue. If the residue does not amount to more than 4 to 5 grams, it is acidified with acetic acid and the boric acid determined by distillation. If considerable residue is present, hydrochloric acid is added to acid reaction, and then the mixture digested with absolute alcohol in a corked flask for ten to fifteen hours, with occasional shaking. The solution is filtered, the residue washed with 95% alcohol, the filtrate diluted with water, 10 cc. of 10% sodium hydroxide solution added and the alcohol

distilled off. A second alcoholic extraction is generally recommended. The final alkaline solution is taken to dryness and gently ignited. The residue is extracted with water, made acid with acetic acid and B_2O_3 determined by distillation.

Carbonates. The material is treated with sufficient acid (M. O. indicator) to liberate all the CO_2 and react with the combined alkali of boric and carbonic acid; it is boiled in a flask with reflux condenser to expel CO_2, ten to fifteen minutes, the solution exactly neutralized with sodium hydroxide, (M. O.), and the liberated boric acid titrated in presence of glycerol and phenolphthalein as usual.

Boric Acid in Milk, Butter, Meat and Other Foods

Milk.[1] One hundred cc. of milk is treated with 1 to 2 grams of sodium hydroxide, and evaporated to dryness in a platinum dish. The residue is thoroughly charred [2] by gently heating; at this stage care must be exercised or loss of boric acid will result; 20 cc. of water are added, the sample heated and hydrochloric acid added drop by drop until all but the carbon has dissolved. The mixture is washed into a 100-cc. flask with as little water as possible, 0.5 gram calcium chloride added, then a few drops of phenolphthalein indicator, then a 10% sodium hydroxide solution until a slight permanent pink color is obtained and finally 25 cc. of lime water. (All P_2O_5 is precipitated as calcium phosphate.) The liquid is made to 100 cc., mixed thoroughly, and then filtered through a dry filter. To 50 cc. of the filtrate, equivalent to 50 cc. of the milk taken, normal sulphuric acid is added until the pink color disappears, then methyl orange indicator is added, followed by more of the standard acid until the yellow color changes to a faint pink. Carbon dioxide is expelled and the liberated boric acid titrated in presence of glycerine, according to the procedure given for evaluation of borax and boric acid, under "Volumetric Determination of Boron."

Butter.[3] Twenty-five grams of butter are weighed out in a beaker and 25 cc. of a sugar sulphuric acid mixture added. (Mix = 6 grams sugar of milk, 4 cc. normal sulphuric acid per 100 cc. of solution.) The beaker is placed in the oven (100° C.) until the fat is melted and the mixture is thoroughly stirred. When the aqueous solution has settled, 20 cc. are pipetted out, phenolphthalein added, the solution brought to boiling and half-normal sodium hydroxide added until a faint pink color is obtained. Ten cc. of neutral glycerine are added and the titration carried on until a permanent pink color appears. The difference between the two titrations multiplied by the factor for equivalent boric acid gives the weight of boric acid in the portion taken.

The determination is not affected by the phosphoric or butyric acid or by the sugar of milk in the butter.

Meat.[4] Ten grams of the chopped meat are mixed in a mortar with 40 to 80 grams of anhydrous sodium sulphate, and dried in the water oven. The mass is powdered, then placed in a flask and 100 cc. of methyl alcohol added and allowed to stand for about twelve hours. The alcohol is distilled into a flask and saved. Fifty cc. more of alcohol are added to the residue and this again distilled into the first distillate. The distillates are made up to 150 cc., a

[1] R. T. Thomson, Glasgow City Anal. Soc. Repts., 1895, p. 3.
[2] The milk residue thoroughly charred will give a colorless solution upon extraction.
[3] H. Droop Richmond and J. B. P. Harrison, Analyst, 27, 197.
[4] C. Fresenius and G. Popp, Chem. Centr., 1897, 2, 69.

50-cc. portion diluted with 50 cc. of water and 50 cc. of neutral glycerine added with phenolphthalein indicator, and the boric acid titrated with twentieth-normal sodium hydroxide.

One cc. N/20 NaOH = 0.0031 gram boric acid, H_3BO_3.

Boric acid in canned goods, sauces, cereals, etc., may be determined by evaporation of the substance with sodium hydroxide and incineration as in case of milk. The sodium hydroxide is neutralized and boric acid titrated as usual.

GRAVIMETRIC DETERMINATION OF BORON

The solubility of boron compounds prevents complete precipitation by any of the known reagents, hence most of the gravimetric methods are indirect.

Distillation as Methyl Borate and Fixation by Lime [1]

This excellent method, worked out by Rosenbladt and Gooch, and highly recommended by Treadwell and Hall, depends upon the fact that the borates of alkaline earths and alkalies give up their boron in the form of the volatile methyl borate (*b.p.*, 65° C.), when they are distilled with absolute methyl alcohol (acetone-free). The methyl borate passed over lime in presence of water is completely saponified, the liberated boric acid combining with the lime to form calcium borate, which may be dried, ignited, and weighed. The increase of the weight of the lime represents the B_2O_3 in the sample.

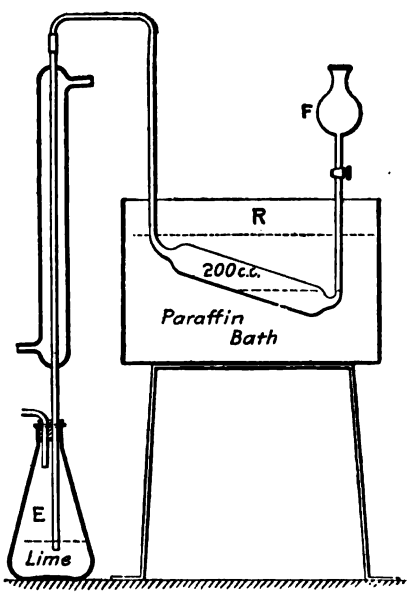

FIG. 8.—Distillation of Methyl Borate.

$$2B(OCH_3)_3+CaO+6H_2O = 6CH_3OH+Ca(BO_2)_2+3H_2O.$$

Procedure. About 1 gram of pure calcium oxide is ignited to constant weight over a blast lamp and then transferred to the dry, Erlenmeyer receiving flask (Fig. 8). The crucible in which the lime was heated and weighed is set aside in a desiccator for later use.

0.2 gram or less of the alkali borates, obtained in solution by a procedure given under "Preparation of the Sample," is treated with a few drops of litmus (or lacmoid), solution and the free alkali neutralized with dilute HCl solution added drop by drop. A drop of dilute sodium hydroxide solution is added and then a few drops of acetic acid. The slightly acid solution is transferred to the pipette-shaped retort *R*, Fig. 8, by means of the attached funnel, *F*, washing out the beaker and funnel with three 2- to 3-cc. portions of water. The stop-

[1] Zeit. f. anal. Chem., 27 (1887, pp. 18, 364). Anal. Chem., Treadwell-Hall, Vol. 2.

cock of the funnel is closed, the apparatus is connected up as shown in the illustration, the paraffine bath, heated to not over 140° C., placed in position and the liquid in the retort distilled into the receiver containing the known amount of lime. When all the liquid has distilled over, the paraffine bath is lowered, the retort allowed to cool for a few minutes, 10 cc. of methyl alcohol (acetone-free) added to the residue in *R* and the contents again distilled by replacing the paraffine bath. The process is repeated three times with methyl alcohol. The contents of the retort (which are now alkaline), are made distinctly acid by addition of acetic acid, and three more distillations made with 100-cc. portions of methyl alcohol, as before. The paraffine bath is now removed, the receiving flask is stoppered, the contents thoroughly mixed by shaking, and set aside for an hour or more for complete saponification of the methyl borate. The contents are now poured into a large platinum dish and evaporated on the water bath at a temperature below the boiling-point of the alcohol. (Loss of boric acid will occur if the alcohol boils.) The adhering lime in the receiving flask is dissolved by wetting its entire surface with a few drops of dilute nitric acid (the flask being inclined and revolved to flow the acid over its sides). The contents are transferred to the dish with a little water and the evaporation repeated. No loss of boric acid will take place at this stage, the alcohol having been removed during the first evaporation. The residue is gently heated to destroy any calcium acetate that may have formed, the cooled borate and lime are taken up with a little water and transferred to the crucible in which the lime was heated and weighed. The material clinging to the dish is dissolved with a little nitric acid (or acetic acid), and washed into the crucible. The contents of the crucible are evaporated to dryness on the water bath, then heated very gently over a flame (the crucible being covered) and finally more strongly. The heating is continued until a constant weight is obtained. The increase of weight of the lime represents the amount of B_2O_3 in the sample.

NOTES. Gooch and Jones worked out a procedure which utilizes sodium tungstate as a retainer of the methyl borate, in place of the lime. This substance is definite in weight, not hydroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. "Methods in Chem. Anal.," p. 204, 1st Ed. Gooch, John Wiley & Sons, Publishers.

The receiving flask has a cork stopper with a hole to accommodate the tube of the condenser and a slit to permit the escape of air from the flask.

Gooch recommends cooling of the receiving flask.

VOLUMETRIC DETERMINATION OF BORON

Titration of Boric Acid in Presence of Mannitol or Glycerol Evaluation of Borax

The method takes advantage of the fact that boric acid reacts neutral to methyl orange (or paranitrophenol), but is acid to phenolphthalein, and may be quantitatively titrated in the presence of mannitol or of glycerol, which prevent the hydrolization of sodium borate. If insufficient mannitol or glycerol are present the color change takes place too soon, the color fading upon addition of more of these substances. The end-point is reached when the further addition of these reagents produces no fading of the color. In the procedure, the alkali is neutralized in presence of methyl orange (or paranitrophenol), and the liberated boric acid is now titrated.

Reactions. $Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3$
$H_3BO_3+NaOH=NaBO_2+2H_2O.$

Procedure. One hundred cc. of the solution containing the borax, prepared according to directions under "Preparation and Solution of the Sample," equivalent to 2 grams of the substance, is taken for analysis.

A. Titration of Combined or Free Alkali. Methyl orange indicator is added and the solution is titrated with normal or half-normal sulphuric acid until the yellow color is replaced by an orange red. (With paranitrophenol the solution becomes colorless.) From this titration the combined alkali, together with any free alkali, is calculated. If free alkali is known to be absent (see note), the amount of borax may be calculated.

One cc. N. $H_2SO_4=0.031$ gram Na_2O, or $=0.1911$ gram $Na_2B_4O_7\cdot10H_2O$, or $=0.101$ gram $Na_2B_4O_7$.

B. Titration of Boric Acid. The liberated boric acid may now be titrated with caustic. This may be accomplished either on the above portion or on a fresh 100-cc. portion (free from methyl orange indicator), to which the amount of acid, required to neutralize the alkali, has been added. Fifty cc. of neutral glycerol or 1 gram of mannitol are added, followed by phenolphthalein indicator. Normal or half-normal sodium hydroxide is added from a burette until a change of color takes place. If methyl orange is present, the color, first becoming yellow, changes to an orange red. In absence of methyl orange the characteristic lavender or purplish pink of alkali phenolphthalein is obtained. More glycerol or mannitol is now added and if the color fades the titration is continued until the addition of these reagents no longer produces this fading of the end-point. From this titration boric acid is calculated and the equivalent borax determined.

One cc. N. $NaOH=0.062$ gram H_3BO_3, equivalent to 0.0505 $Na_2B_4O_7$, or 0.0955 $Na_2B_4O_7\cdot10H_2O$.

Factors. Na_2O to $Na_2B_4O_7=3.2581$, reciprocal $=0.3069$.
Na_2O to $Na_2B_4O_7\cdot10H_2O=6.1638$, recip. $=0.1622$.
Na_2O to $Na_2CO_3=1.7097$, recip. $=0.5849$.
Na_2O to $Na_2CO_3\cdot10H_2O=4.6155$, recip. $=0.2167$.

NOTES. In borax (free from excess B_2O_3 or Na_2O), the acid titration is half the subsequent alkali titration (factor, acid to borax $=0.1911$, alkali to borax $=0.0955$).

If the acid titration exceeds this proportion, alkali other than that combined with boric acid is indicated; if the alkali titration is greater than twice the acid titration, free boric acid is indicated.

The glycerol should be made neutral with N/10 NaOH before use, in case it contains free fatty acids.

Mannitol is a solid and has some advantages over glycerol; it gives a sharper end-point, is less apt to contain free acids and does not appreciably alter the bulk of the solution to which it is added. (L. C. Jones, C. N., 80, 65, 1899).

N.B. Paper on use of mannitol and glycerol in determining boric acid, by R. T. Thomson, J. S. C. I., 12, 432.

Example. By actual test 2 grams $Na_2B_4O_7 \cdot 10H_2O$ required 10.66 cc. N. $H_2SO_4 = 10.66 \times 0.1911 = 2.037$ gram $Na_2B_4O_7 \cdot 10H_2O$. The liberated H_3BO_3 required 21.39 cc. of N. NaOH $= 21.39 \times 0.0955 = 2.043$ gram $Na_2B_4O_7 \cdot 10H_2O$. The borax had lost a small amount of water of crystallization, hence the high results when calculated to $Na_2B_4O_7 \cdot 10H_2O$.

EVALUATION OF BORIC ACID

One hundred cc. of the solution, prepared as directed under "Preparation of the Sample," equivalent to 2 grams of the original material, is treated with 50 cc. of glycerol or 1 gram of mannitol, and the acid titrated with standard caustic, in presence of phenolphthalein indicator according to the procedure given in *B*, under "Evaluation of Borax."

One cc. normal acid contains 0.062 gram H_3BO_3, hence the cc. of caustic required multiplied by 0.062 = grams boric acid.

Examples. Two grams H_3BO_3 by actual test required 32.1 cc. N. NaOH $= 32.1 \times .062 = 1.99$ grams H_3BO_3.

Detection of Minute Amounts of Boron.

Robin's Test for Boron. To a few drops of the aqueous solution under examination (slightly acidified with HCl) are added two drops of a tincture of mimosa flowers, and the mixture evaporated to dryness on the water bath. The residue is treated with dilute ammonia water, whereupon in presence of boric acid, a rose pink to blood red color develops, according to the amount present. L. Robin claims that as little as 0.0001 milligram may be detected in presence of nitrates, chlorides, iodides, or calcium sulphate. Organic acids and sodium phosphate interfere. The reagent is prepared by extracting the mimosa flowers with ethyl alcohol. The extract is protected from the light.

BROMINE

WILFRED W. SCOTT

Br, *at.wt.* 79.92; *sp.gr.* 3.1883°; *m.p.* −7.3°; *b.p.* 58.7° C.; *acids*, HBr, HBrO, $HBrO_3$

DETECTION

Silver Nitrate solution precipitates silver bromide, AgBr, light yellow from solutions containing the bromine anion. The precipitate is insoluble in dilute nitric acid, but dissolves with difficulty in ammonium hydroxide and is practically insoluble in ammonium carbonate solution (distinction from AgCl).

Carbon Disulphide or Carbon Tetrachloride shaken with free bromine solution, or with a bromide to which a little chlorine water has been added (a large excess of chlorine must be avoided, as this forms BrCl compound), will absorb the bromine and become a reddish-yellow color, or, if much bromine is present, a brown to brownish-black. In the latter case a smaller sample should be taken to distinguish it from iodine.

Bromates are first reduced by a suitable reducing agent such as cold oxalic acid, sodium nitrite, hydrochloric acid, etc., and the liberated bromine tested as directed above. *Silver nitrate* added to bromates in solution precipitates $AgBrO_3$, which is decomposed by hydrochloric acid to bromine gas.

Barium Chloride precipitates $Ba(BrO_3)_2$, which is reduced readily to bromine as directed above.

Magenta Test for Bromine.[1] The test reagent is made by adding 10 cc. of 0.1% solution of magenta to 100 cc. of 5% solution of sulphurous acid and allowing to stand until colorless. This is the stock solution. Twenty-five cc. of this reagent is mixed with 25 cc. of glacial acetic acid and 1 cc. of sulphuric acid. Five cc. of this is used in the test.

Test. Five cc. of the magenta reagent is mixed with 1 cc. of the solution tested. Chlorine produces a yellow color. Bromine gives a reddish-violet coloration. The colored compound in each case may be taken up with chloroform or carbon tetrachloride and a colorimetric comparison made with a standard.

In halogen mixes, iodine is first eliminated by heating with an iron per salt. Bromine is now liberated by adding sulphuric acid and potassium chromate. A glass rod with a pendant drop of sodium hydroxide is held in the vapor to absorb bromine, and the drop then tested with the magenta reagent. After iodine and bromine are eliminated, chlorine may be tested by heating the substance with potassium permanganate, which liberates this halogen.

[1] G. Denigès and L. Chelle. Ann. Chim. anal., 1913, **18**, 11–15; The Analyst, 1913, 119.

ESTIMATION

Bromine never occurs free in nature. It is found chiefly combined with the alkalies and the alkaline earths, hence occurs in many saline springs and is a by-product of the salt industry. It is found in silician zinc ores, Chili saltpeter, in sea water (probably as $MgBr_2$), in marine plants. Traces occur in coal, hence in gas liquors.

The substance is used in metallurgy, the arts, and medicine. It is a valuable oxidizing agent for the laboratory.

Preparation and Solution of the Sample

The following facts regarding solubility should be remembered: The element bromine is very soluble in alcohol, ether, chloroform, carbon disulphide, carbon tetrachloride, concentrated hydrochloric acid and in potassium bromide solution. One hundred cc. of water at 0° C. is saturated with 4.17 grams of bromine, and at 50° C. with 3.49 grams. The presence of a number of salts increases its solubility in water, e.g., $BaCl_2$, $SrCl_2$, etc.

NOTE. The element is a dark, brownish-red, volatile liquid, giving off a dark reddish vapor with suffocating odor, irritating the mucous membrane (antidote dil. NH_4OH, ether), very corrosive. Acts violently on hydrogen, sulphur, phosphorus, arsenic, antimony, tin, the heavy metals, and on potassium, but has no action on sodium, even at 200° C. Bleaches indigo, litmus, and most organic coloring matter. It is a strong oxidizing agent. Bromine displaces iodine from its salts, but is displaced by chlorine from its combinations.

Bromides are soluble in water, with the exception of silver, mercury, lead, and cuprous bromides.

Bromates are soluble in water with the exception of barium and silver bromates and some basic bromates.

Decomposition of Organic Matter for Determination of Bromine. The substance is decomposed with nitric acid in presence of silver nitrate in a bomb combustion tube by the Carius method described in the chapter on Chlorine, under "Preparation and Solution of the Sample." The residue, containing the halides, is dissolved in warm ammonia water, and filtered, as stated. The filtrate and washings are acidified with nitric acid, heated to boiling and the silver bromide settled in the dark, then filtered through a weighed Gooch crucible, the washed precipitate dried at 130° C. and weighed as AgBr.

In presence of two or three halogens the lime method is recommended, as given in the chapter on chlorine, page 122.

Salts of Bromine. The ready solubility of bromides and bromates has been mentioned. A water extract is generally sufficient. Insoluble salts are decomposed by acidifying with dilute sulphuric acid and adding metallic zinc. The filtrate contains the halogens.

SEPARATIONS

Separation of Bromine from the Heavy Metals. Bromides of the heavy metals are transposed by boiling with sodium carbonate, the metals being precipitated as carbonates and sodium bromide remaining in solution.

Separation of Bromine from Silver (AgBr) and from Cyanides (AgCN). The silver salts are heated to fusion. The mass is now treated with an excess

of zinc and sulphuric acid, the metallic silver and the paracyanogen filtered off and the bromine determined in the filtrate.

Separation of Bromine from Chlorine or from Iodine. Details of the procedure for determining the halogens in presence of one another is given in the chapter on Chlorine, page 130. Free bromine is liberated when the solution of its salt is treated with chlorine.

Separation of Bromine from Iodine.[1] The neutral solution containing the bromide and iodide is diluted to about 700 cc. and 2 to 3 cc. of dilute sulphuric acid, 1 : 1, added, together with about 10 cc. of 10% sodium nitrite, $NaNO_2$, solution. (Nitrous acid gas may be passed through the solution in place of adding sodium nitrite, if desired.)[2] The solution containing the halides is boiled until colorless and about twenty minutes longer, keeping the volume of solution above 600 cc. 0.5 gram KI may be decomposed and the iodine expelled from the bromide in half an hour. The bromine is precipitated from the residue remaining in the flask by addition of an excess of silver nitrate and determined as silver bromide.

The procedure for determining iodine is given in the chapter on this subject.

GRAVIMETRIC METHODS

Precipitation as Silver Bromide

The general directions for determination of hydrochloric acid and chlorides apply for determining hydrobromic acid and bromides.

I. Hydrobromic Acid and Bromides of the Alkalies and Alkaline Earths.

Procedure. The bromide in cold solution is made slightly acid with nitric acid and then silver nitrate added slowly with constant stirring until a slight excess is present. The mixture is now heated to boiling and the precipitate settled in the dark, then filtered through a weighed Gooch crucible, and washed with water containing a little nitric acid and finally with pure water to remove the nitric acid. After ignition the silver bromide is cooled and weighed as AgBr.

$$AgBr \times 0.4256 = Br, \text{ or } \times 0.6337 = KBr.$$

II. Heavy Metals Present.

If heavy metals are present it is not always possible to precipitate silver bromide directly. The heavy metals may be removed by precipitation with ammonia, sodium hydroxide or carbonate and the bromide then determined in the filtrate as usual.

VOLUMETRIC METHODS

Free hydrobromic acid may be titrated with standard alkali exactly as is described for the determination of hydrochloric acid in the chapter on Acids. One cc. normal caustic solution is equivalent to 0.08093 gram HBr.

[1] F. A. Gooch and J. R. Ensign, Am. Jour. Sci., (3), xl, 145.

[2] Nitrous acid gas is generated by dropping dilute H_2SO_4, by means of a separatory funnel onto sodium nitrite in a flask.

Determination of Free Bromine. Potassium Iodide Method

The method depends upon the reaction $KI+Br=KBr+I$.

Procedure. A measured amount of the sample is added to an excess of potassium iodide, in a glass-stoppered bottle, holding the point of the delivering burette just above the potassium iodide solution. The stoppered bottle is then well shaken, and the liberated iodine titrated with standard thiosulphate solution.

One cc. of N/10 thiosulphate, $Na_2S_2O_3=0.007992$ gram Br.

Determination of Bromine in Soluble Bromides. Liberation of Bromine by Addition of Free Chlorine

When chlorine is added to a colorless solution of a soluble bromide, bromine is liberated, coloring the solution yellow. At boiling temperature the bromine is volatilized, the liquid becoming again colorless. When the bromide is completely decomposed and bromine expelled, further addition of chlorine produces no color reaction. $KBr+Cl=KCl+Br$.

Procedure. The solution containing the bromide is heated to boiling and standard chlorine water added from a burette (protected from the light by being covered with black paper), the tip of the burette being held just above the surface of the hot bromide solution to prevent loss of chlorine. The reagent is added in small portions until finally no yellow coloration is produced. From the value per cc. of the chlorine reagent the bromine content is readily calculated.

Standard Chlorine Water. The reagent is made by diluting 100 cc. of water saturated with chlorine to 500 cc. This solution is standardized against a known amount of pure potassium bromide (dried at 170° C.), the same amount of bromide being taken as is supposed to be present in the solution examined. The value per cc. of the reagent is thus established.

Silver-Thiocyanate-Ferric Alum Method. (Volhard)

The procedure is the same as that used for the determination of chlorine. The bromide solution is treated with an excess of tenth-normal silver nitrate solution, and the excess of this reagent determined by titration with ammonium thiocyanate, using ferric alum indicator. One cc. of the thiocyanate should be equivalent to 1 cc. of silver nitrate solution. The formation of the red ferric thiocyanate indicates the completed reaction. (Consult the procedure in the chapter on Chlorine, page 125.)

One cc. of N/10 $AgNO_3=0.007992$ gram Br.

Determination of Traces of Bromine

By means of the magenta reagent, described under "Detection," small amounts of bromine may be determined colorimetrically.

To 5 cc. of the solution is added 0.2 cc. of strong hydrochloric acid, 1 cc. of concentrated sulphuric acid, 1 cc. of the stock magenta reagent and 0.2 cc. of a 10% solution of potassium chromate, shaking the mixture with addition

of each reagent, and without cooling, 1 cc. of chloroform is added. Comparison is made with a standard sample containing a known amount of bromide.[1]

NOTE. A solution containing 0.001 gram bromine per liter has a violet to reddish-violet color.

Determination of Bromates by Reduction with Arsenous Acid and Titration of the Excess[2]

Bromic acid may be reduced by arsenous acid in accordance with the reaction $3H_3AsO_3+HBrO_3=3H_3AsO_4+HBr$. In the process a considerable excess of arsenous acid is added, the excess titrated with iodine and the bromate calculated.

Procedure. The sample of bromate, dissolved in water, is treated with a considerable excess of N/10 arsenous oxide (dissolved in alkali hydrogen carbonate) reagent, the solution then acidified with 3 cc. to 7 cc. of dilute sulphuric acid (1 : 1) and diluted to a volume not exceeding 200 cc. After boiling for ten minutes, the free acid is neutralized with alkali hydrogen carbonate ($NaHCO_3$ or $KHCO_3$) and the excess of arsenite titrated with N/10 iodine.

Let x cc. equal the difference between the two titrations with N/10 iodine (i.e. of total arsenite minus excess arsenite) and w equal the weight of bromate desired, then

$$w=\left(\frac{x\text{ cc.}\times\text{mol. wt. }RBrO_3}{6\times10\times1000}\right)\text{milligrams.}$$

ANALYSIS OF CRUDE POTASSIUM BROMIDE AND COMMERCIAL BROMINE

Determination of Chlorine, Combined or Free

This is the principal impurity present and its estimation is concerned here. Andrews' modification of Bugarszk's method[3] is as follows:

Procedure. The following amount of sample and reagents should be taken.

Approx. per cent Impurity if KCl Present is	Amount Substance to be Taken, Gram.	Iodate Solution 1/5 N. Required: cc.	⅔N. HNO_3 Required, cc.
Over 5	0.6	36	20
1.5 to 5	1.8	96	26
0.2 to 1.5	3.6	186	35

[1] G. Denigés and L. Chelle, Ann. Chem. anal., 1913, 18–15; Analyst, 1913, p. 119. By means of the magenta reagent it is possible to detect bromine in the ash of plants, beet root, spinach, etc. The organic substance may be decomposed by heating in a combustion tube. Filter paper moistened with the reagent and held in the fumes of the organic substances gives the characteristic test if bromine is present.

[2] Method of F. A. Gooch and J. C. Blake, Am. Jour. Sci., **14**, Oct., 1902. Procedure communicated to the Editor by Prof. Gooch.

[3] Jour. Am. Chem. Soc., 1907, **29**, 275–283; Zeits. anorg. Chem., 1895, **10**, 387.

The mixture is gently heated to boiling in a long-necked Kjeldahl flask, inclined at an angle of 30°, potassium iodate solution added, then nitric acid and sufficient water to make the volume about 250 cc. The boiling is continued until bromine is expelled (test steam with 2% KI solution rendered faintly acid with hydrochloric acid). The mixture is boiled down to not below 90 cc. Now 1 to 1.5 cc. of 25% phosphorus acid are added and the mixture boiled for five minutes after all the iodine has been expelled. The colorless liquid is cooled, mixed with a slight excess of 1/20 or 1/50 normal silver nitrate solution (according to the proportion of chloride), the excess of silver nitrate then determined by titration with standard thiocyanate with ferric nitrate as indicator. (See procedure for silver-thiocyanate-ferric alum method of Volhard for determination of chlorine, page 125.)

Determination of Chlorine in Crude Bromine

Three grams of bromine (or more if less than 0.5% chlorine is present) in 50 cc. of 4% potassium iodide solution in a glass-stoppered flask (cooled in ice during hot weather) are shaken and then transferred to a Kjeldahl flask. Sixty cc. of 1/5 N. KIO_3 solution and 24 cc. 2N. HNO_3 introduced, the solution diluted to 250 cc. and chlorine determined as directed above.

CADMIUM

WILFRED W. SCOTT

Cd, *at.wt.* 112.4; *sp.gr.* 8.642; *m.p.* 320.9°[1]; *b.p.* 778° C.; *oxide,* CdO

DETECTION

Cadmium is precipitated by hydrogen sulphide from an acid solution as yellow cadmium sulphide, CdS. The precipitate is insoluble in ammonium sulphide (distinction from arsenic, antimony, and tin), but dissolves upon addition of hot nitric acid (separation from mercury). Upon addition of sulphuric acid and expulsion of nitric by taking the solution to SO_3 fumes, and dilution with water, cadmium remains in solution (lead is precipitated, $PbSO_4$). Bismuth is precipitated by ammonium hydroxide and removed by filtration. Potassium cyanide is added to prevent the precipitation of copper sulphide; and hydrogen sulphide is led into the solution, whereupon cadmium precipitates as yellow CdS.

Cadmium gives a brilliant spectrum of green and blue lines.

Blowpipe Tests. Heated on charcoal in the reducing flame, cadmium gives a brown incrustation. The residue is volatile in the reducing flame.

ESTIMATION

The element occurs combined as the sulphide in small quantities. In the mineral greenockite it occurs as the principal element. As it occurs in practically all zinc ores and is found in most commercial zinc, it is determined in the analysis of these substances. It is a by-product of lead and zinc smelting. The element is determined in certain alloys, especially those used for trial plates for silver coinage. It is determined in paint pigments; e.g., CdS, yellow.

Preparation and Solution of the Sample

The metal is slowly soluble in hot, moderately dilute hydrochloric acid or sulphuric acid, much more readily in nitric acid. It is soluble in ammonium nitrate. The oxide is readily soluble in acids.

Treatment of Ores

Sulphides are best dissolved by treating 0.5 to 1 gram of the finely powdered ore with 15 to 20 cc. of strong hydrochloric acid and 10 cc. of strong nitric acid. After standing on the water bath for ten to fifteen minutes, the solution is boiled until the sulphides are decomposed, additional hydrochloric being added if necessary. Unless silica is known to be absent the solution is taken to dryness and the residue dehydrated in the air oven for an hour. Five to ten cc. of strong hydrochloric acid and about 25 cc. of water are added and the

[1] Cir. 35 (2d Ed.), U. S. Bureau of Standards.

mixture heated to boiling. The residue of silica should appear white. This is filtered off and cadmium determined in the filtrate after making the necessary separations.

If lead is present it is advisable to add 5–6 cc. of concentrated sulphuric acid to the cooled solution after the hydrochloric-nitric acid treatment and to evaporate to SO_3 fumes. After cooling, 50 cc. of water are added and the mixture heated to boiling, then placed on the steam bath until any iron present has completely dissolved. Silica and lead are now filtered off and the filtrate treated as directed under "Separations."

Carbonates may be dissolved by hydrochloric acid alone. Evaporation to dryness is necessary if silica is present.

Alloys are best dissolved in hydrochloric and nitric acids, followed by addition of sulphuric acid, and nitric acid then expelled by evaporating the solution to SO_3 fumes.

SEPARATIONS

Removal of Silica. The procedure has been given under "Preparation and Solution of the Sample."

Separation from the Ammonium Sulphide Group, the Alkaline Earths and the Alkalies. The solution, acidified with 2 cc. of concentrated sulphuric acid or about 5 cc. of strong hydrochloric acid per 100 cc., is treated with hydrogen sulphide to saturation. The precipitate, containing cadmium sulphide with other members of the group that were present in the original solution, is filtered off and washed with hydrogen sulphide water slightly acidulated with hydrochloric acid.

Removal of Arsenic, Antimony, and Tin. Treatment in Absence of Copper. The precipitate is rinsed from the filter into the beaker as completely as possible with no more water than is necessary. The beaker is placed under the filter and cold solution of potassium hydroxide (20%) is poured onto the filter. (Sodium hydroxide will do.) Arsenic, antimony, and tin will dissolve and leave cadmium sulphide. A dark-colored residue indicates the presence of bismuth, lead, and less frequently, of mercury.

Treatment in Presence of Copper. A strong solution of potassium cyanide may be used in place of a fixed alkali hydroxide. By this treatment, the copper is removed along with arsenic, antimony, and tin.

If the precipitate is yellow or orange-colored,[1] it is dissolved in hydrochloric acid, after thorough washing with hydrogen sulphide water, and the solution treated according to one of the procedures given later.

Removal of Lead and Bismuth. Should the above precipitate appear dark-colored, lead, bismuth, and possibly mercury are indicated. In the preliminary treatment of the ore with sulphuric acid, the lead is generally completely removed as lead sulphate, but traces may be present in the filtrate. The moist precipitate and filter are placed in a flask and 10 cc. of strong hydrochloric acid added, with an equal amount of water. The mixture is boiled until the cadmium sulphide dissolves, the H_2S gas being driven out of the solution. The solution, diluted with 25 cc. of water, is filtered, and the filter washed with hot water. Any dark residue may be rejected. The filtrate is diluted somewhat and then sodium carbonate added in slight excess, followed by 1 or 2 grams of potassium cyanide. After digesting for some time at a gentle heat

[1] Cadmium sulphide precipitated from a sulphuric acid solution is orange-colored.

the mixture is filtered and washed with cold water. Bismuth and lead remain on the filter as carbonates. H_2S is now passed into the filtrate, diluted if necessary. This should precipitate pure cadmium sulphide, unless mercury is present. The residue is washed with hydrogen sulphide water, and then dissolved in hydrochloric acid.

Separation of Cadmium from Mercury. This separation is seldom required. The procedure is based upon the insolubility of mercury sulphide in hot dilute nitric acid, whereas cadmium sulphide is readily soluble. The two sulphides are boiled with nitric acid, 1 : 3, filtered and the residue washed with hot water. The filtrate is evaporated with a little sulphuric acid to small volume on the hot plate and then to SO_3 fumes. (Spattering during the last stages of removal of water will cause loss unless the recepticle is covered.) The cooled residue is taken up with water and if any insoluble matter remains it is filtered off. Cadmium is now determined in the solution.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF CADMIUM

Determination as Cadmium Sulphate, $CdSO_4$

The hydrochloric acid solution of cadmium obtained under the section on isolation of the cadmium is evaporated to dryness on the water bath in a weighed platinum crucible or dish. The residue is covered with a slight excess of dilute sulphuric acid, the solution again evaporated as far as possible on the water bath, and finally the excess sulphuric acid expelled by gently heating. This final stage is best accomplished by placing the crucible in a larger one, provided with an asbestos ring to separate the two. The outer crucible may now be heated to redness without danger of decomposing the cadmium sulphate. The heating is continued until no more fumes of sulphuric acid are evolved. The residue is weighed as cadmium sulphate, $CdSO_4$.

$$CdSO_4 \times 0.5392 = Cd.$$

Electrolytic Determination of Cadmium

This method for determination of cadmium is exceedingly accurate. The procedure recommended by Treadwell [1] gives excellent results.

Procedure. A drop of phenolphthalein is added to the cadmium sulphate solution (obtained by evaporating the hydrochloric acid solution with sulphuric acid to SO_3 fumes), then a solution of pure caustic soda until a permanent red color is obtained. A strong solution of potassium cyanide is now cautiously added with constant stirring, until the cadmium hydroxide precipitate just dissolves (an excess should be avoided). The solution is diluted to 100–150 cc. with water and electrolyzed in the cold, using a gauze cathode, the current being 0.5 to 0.7 ampere and the electromotive force 4.8 to 5 volts. At the end of five or six hours the current is increased to 1–1.2 amperes, and the solution electrolyzed for an hour more.

The liquid is quickly poured off, or better, the beaker lowered, and another

[1] Treadwell and Hall, Analytical Chem., Vol. II. Beilstein and Jawein, Ber., **12**, 446.

of water substituted. The deposited metal is then washed by dipping the cathode in alcohol and finally in ether. After drying at 100° C., the cooled cathode is weighed. The increase of weight represents the deposited metal, cadmium.

NOTES. Before washing and discontinuing the current, it is advisable to add a little water to raise the level of the liquid and continue the electrolysis to ascertain whether the deposition is complete.

Traces of cadmium may be estimated in the above solution by saturating this with H_2S and comparing the yellow-colored colloidal cadmium sulphide solution with a known quantity of cadmium and the same amounts of potassium hydroxide and cyanide as in the solution tested.

VOLUMETRIC DETERMINATION OF CADMIUM

Titration of Cadmium Sulphide with Iodine.[1]

The titration of cadmium sulphide with standard iodine in a hydrochloric acid solution is the same as the procedure given for determination of sulphur by the evolution method, the following reaction taking place:

$$CdS+2HCl+I_2=CdCl_2+2HI+S.$$

Procedure. Cadmium having been isolated as the sulphide according to the standard procedures given, the precipitate is washed and allowed to drain on the filter. The filter, together with the sulphide, is placed in a beaker or an Erlenmeyer flask, water added, and the whole shaken to break up the precipitate. A moderate quantity of hydrochloric acid is added and the solution titrated with standard N/5 or N/10 iodine solution. Towards the end a little starch solution is added and the titration continued until the excess of iodine colors the solution blue. If preferred, an excess of iodine solution may be added and the excess determined by a back-titration with standard thiosulphate solution.

One cc. N/10 iodine = 0.00562 gram cadmium.

[1] P. von Berg (Z. a. C., **26**, 23) transfers the precipitate and filter to a stoppered flask, expels the air with CO_2 and by boiling and then titrates in an hydrochloric acid solution. Experiments by the author have shown this caution to be unnecessary.

CALCIUM

WILFRED W. SCOTT

Ca, *at.wt.* 40.07; *sp.gr.* 1.5446$^{29°}$; *m.p.* 810° [1] C.; *oxide*, CaO

DETECTION

In the usual course of qualitative and quantitative analysis calcium passes into the filtrates from the elements precipitated by hydrogen sulphide in acid and alkaline solutions (Ag, Hg′, Hg″, Pb, Cu, Cd, As, Sb, Sn, Fe, Cr, Al, Mn, Ni, Co, Zn, etc.), and is precipitated from an ammoniacal solution by ammonium carbonate as calcium carbonate, along with the carbonates of barium and strontium. The separation of calcium from barium and strontium is considered under Separations. The oxalate of calcium is the least soluble of the alkaline-earth group.[2] All, however, are soluble in mineral acids. Calcium oxalate may be precipitated from weak acetic acid solution by ammonium oxalate.

Flame Test. The flame of a Bunsen burner is colored yellowish red when a platinum wire containing calcium salt moistened with concentrated hydrochloric acid is held in the flame.

Spectrum. An intense orange and green line with a less distinct violet line. Note chart of the spectra of the alkaline earths. Plate II.

See chapter on Barium under Separations—Preliminary Tests, page 52.

ESTIMATION

The determination of calcium is required in complete analyses of ores. It is of special importance in the analysis of mortar, cement, bleaching powder, plaster of Paris, certain paint pigments such as phosphorescent paint, CaS. The determination is required in the analysis of water.

Calcium occurs in the following substances: as carbonate in limestone, marble, chalk, Iceland spar, shells, coral, pearl. Together with magnesium it is found in dolomite. It occurs as sulphate in anhydrite, gypsum, alabaster, selenite; as silicate in the mineral wollastonite, $CaSiO_3$; as phosphate in phosphorite, $Ca_3(PO_4)_2$, also in bones and in apatite, $3Ca_3(PO_4)_2 \cdot CaF_2$; as fluoride in fluorspar, CaF_2. As oxalate it occurs in plant cells. It is found in nearly all mineral springs, artesian wells, and river waters, principally as bicarbonate of calcium, $CaHCO_3$.

Preparation and Solution of the Sample

The oxide, hydroxide, and salts of calcium are soluble in acids with the exception of gypsum and certain silicates which require fusion with sodium carbonate or bicarbonate followed by an hydrochloric acid extraction.

[1] Cir. 35 (2d Ed.) U. S. Bureau of Standards.

[2] Solubility: $CaC_2O_4 \cdot H_2O = 0.000554$ gram per 100 cc. H_2O. $BaC_2O_4 \cdot H_2O = 0.0093$ gram. $SrC_2O_4 \cdot H_2O = 0.0051$ gram. $MgC_2O_4 2H_2O = 0.07$ gram.

Solution of Limestones, Dolomites, Magnesites, Cements, Lime, etc. One gram of the powdered material is digested in a 250-cc. beaker with 20 cc. of water, 5 cc. of concentrated hydrochloric acid, and 2 or 3 drops of nitric acid (sp.gr. 1.42). The beaker is covered to prevent loss by effervescence. When the violent action has subsided, the sample is placed on a hot plate and boiled for a few minutes. The watch-glass is rinsed into the beaker and the solution filtered. The residue is washed, dried and ignited in a platinum crucible, and then fused with a little sodium carbonate or bicarbonate. The cooled fusion is dissolved in hot dilute hydrochloric acid, the liquid added to the main solution and calcium determined by precipitation as calcium oxalate, after removal of silica, iron, alumina, etc.

Solution of Gypsum, Plaster of Paris, and Sulphates of Lime, etc. The treatment of the sample is similar to the one given above with the exception that it is advisable to add a larger amount of strong hydrochloric acid, e.g., about 20 to 25 cc. If barium sulphate is present it is indicated by the clouding of the solution, upon acidifying the water extract of the carbonate fusion.

Silicates. Solution of silicates is best obtained by direct fusion of 1 gram of the powdered material with 4 to 5 grams of sodium carbonate, in a platinum crucible. The cooled melt is now covered with water and dissolved with hydrochloric acid according to the standard procedure for carbonate fusions. The hydrochloric acid solutions are taken to dryness and the silica dehydrated in an oven at 110° C. for an hour and then the residue is extracted with dilute hydrochloric acid and filtered. The filtrate contains iron, alumina, magnesium, lime, etc.

Chlorides, Nitrates, and Other Water-soluble Salts. These are dissolved in water slightly acidified with hydrochloric acid.

Sulphides, Pyrites Ore, etc. The ore should be oxidized with bromine or by roasting, previous to the acid treatment.

SEPARATIONS

Removal of Silica. The solution obtained by one of the above procedures is evaporated to dryness and the silica dehydrated at 110° C. for an hour. The residue is now extracted with dilute hydrochloric acid. Silica remains insoluble and may be filtered off. The solution contain lime, together with iron, alumina, magnesia, etc., as chlorides.

Removal of Iron and Alumina. The filtrate from the silica residue is treated with a few drops of nitric acid and boiled to oxidize the iron. Ammonia is now added cautiously until the solution just smells of it (a large excess over that required to neutralize the acid and combine with iron and alumina, will tend to dissolve $Al(OH)_3$). The precipitated hydroxides are allowed to settle and then filtered hot through a rapid filter and washed with hot water. Calcium, together with magnesium, is in solution and passes into the filtrate.

Removal of Copper, Nickel, Cobalt, Manganese, Zinc, and Elements Precipitated as Sulphides in Acid and Alkaline Solutions. This separation is required seldom in lime-bearing ores. In analysis of pyrites and certain other ores, containing members of the hydrogen sulphide and ammonium sulphide groups, the removal of these impurities is necessary.

The solution from the residue of silica is made slightly ammoniacal and H_2S passed into the solution to saturation (or ammonium sulphide may be

added). The precipitated sulphides are filtered off from the solution heated to boiling. The filtrate containing the calcium is boiled down to 50 to 75 cc. and the precipitated sulphur removed by filtration. Calcium is determined in the filtrate by precipitation with ammonium oxalate or oxalic acid according to directions given later.

Separation of Calcium from Magnesium and the Alkalies. In the presence of considerable amounts of calcium and comparatively small quantities of magnesium the oxalate method of precipitating calcium, in presence of ammonium chloride, is generally sufficient for precipitating calcium free from magnesium and the alkalies. In analysis of dolomite, $MgCO_3 \cdot CaCO_3$, and of samples containing comparatively large amounts of magnesium, a double precipitation of calcium is generally necessary for removal of occluded magnesium.

Separation of Calcium from Barium and from Strontium. The alkaline earths are converted to nitrates, all moisture expelled by heat, and calcium nitrate extracted from the insoluble nitrates of barium and strontium by a mixture of anhydrous ether and absolute alcohol, in equal parts, or by boiling the dry nitrates in amyl alcohol (*b.p.*, 137.8° C.). Details of the procedure are given under Separations of the Alkaline Earths in the chapter on Barium, page 53.

Phosphate Rocks, Calcium Phosphate, etc.[1]

Determination of Lime in Presence of Phosphates, Iron, and Alumina. Should phosphoric acid be present in the solution, calcium will be precipitated as a phosphate upon making the solution neutral or slightly alkaline with ammonia, and will remain with iron and alumina precipitates.

Precipitation of Calcium Oxalate in Presence of Iron and Alumina. The solution containing the phosphates freed from silica is oxidized by boiling with nitric acid as usual. Ammonia water is added to the cooled solution until a slight precipitate forms, and then citric acid is added in sufficient quantity to just dissolve the precipitate. If this does not readily occur, additional ammonia is added, followed by citric acid until the solution clears, then about 15 cc. of citric acid in excess. The solution is diluted to 200 cc. and heated to boiling. Calcium oxalate is now precipitated by addition of ammonium oxalate. Iron and alumina remain in solution.

Citric acid is made by dissolving 70 grams of the acid, $H_3C_6H_5O_7 \cdot H_2O$, in a liter of water.

Wagner's Solution. In place of citric acid, the following solution may be used. Twenty-five grams of citric acid and 1 gram of salicylic acid are dissolved in water and made to 1000 cc. Twenty-five to 50 cc. of this reagent is effective in preventing precipitation of iron and alumina.

[1] Zeit. für Angewandte Chemie, 34, 776, Aug., 1898.

GRAVIMETRIC DETERMINATION OF CALCIUM

Precipitation of Calcium Oxalate and Ignition to Calcium Oxide

Calcium oxalate is precipitated from feebly ammoniacal solutions or from solutions acidified with acetic, oxalic, citric, or salicylic acids, by means of ammonium oxalate. The presence of ammonium chloride hinders precipitation of magnesium and does not interfere with that of calcium. If, however, much magnesium (or sodium) is present it will contaminate the calcium precipitate so that a second precipitation is necessary to obtain a pure product. The compound formed from hot solutions is crystalline or granular and filters readily, whereas the flocculent precipitate formed in cold solutions does not. Calcium oxalate, $CaC_2O_4 \cdot H_2O$,[1] decomposes at red heat to CaO, in which form it is weighed.

Procedure. If the calcium determined is in the filtrate from previous groups, hydrogen sulphide is expelled by boiling and the precipitated sulphur filtered off, the solution having been concentrated to about 200 cc. The filtrate should contain sufficient ammonium chloride to hold magnesium in solution in presence of ammonium oxalate (i.e, about 10 grams NH_4Cl per 0.0015 gram MgO per 100 cc. of solution.)[2] If not already present, the chloride is added in sufficient amount, and the solution diluted to about 400 cc.

Precipitation. The solution is heated to boiling and 10 cc. of acetic acid added to the neutral mixture. Fifteen cc. or more of a saturated solution of oxalic acid[3] is added and after five minutes a slight excess of ammonia. The solution is allowed to cool an hour or so, the clear solution decanted through a 10-cm. filter and the precipitate washed three times by decantation and finally on the filter with dilute ammonia (1 : 10), or 1% ammonium oxalate.

To remove clinging impurities (Na or Mg) the precipitate is dissolved in dilute nitric acid (1 : 4) and the filtrate collected in the beaker in which the first precipitation was made. The solution is heated to boiling after addition of a few drops of oxalic acid and sufficient ammonium hydroxide to make the solution slightly alkaline. The precipitated oxalate is allowed to settle, filtered and washed as in the first precipitation, the oxalate adhering to the sides of the beaker being carefully "copped" out. The oxalate is ignited wet in a weighed crucible, the heat being low at first, until the filter has charred and then to the full heat of the Méker blast lamp. Fifteen minutes of blasting should be sufficient to obtain constant weight. If the precipitate is large a second igntion is advisable to insurre the complete decomposition of the oxalate and carbonate to oxide.

The crucible is cooled in a desiccator and weighed as soon as possible.[4]

Factors. $CaO \times 0.7146 = Ca$, or $\times 1.7847 = CaCO_3$, or $\times 2.8908 = Ca(HCO_3)_2$, or $\times 2.428 = CaSO_4$.

[1] Calcium oxalate dried at 100 = $CaC_2O_4 \cdot H_2O$. Heated to 200° C. = = CaC_2O_4. At 500° C. the oxalate begins to decompose, free carbon is liberated, and calcium carbonate begins to form. At bright red heat carbon burns off and the carbonate is completely decomposed to the oxide and CO_2.

[2] Mellor, "A Treatise on the Ceramic Industries," 213 (1913).

[3] Approximately 8.6% at 20° C. About five times as much ammonium oxalate as is required for combination with calcium and magnesium should be added to the solution.

[4] Calcium oxide absorbs moisture and CO_2 from the air.

Other Methods. Gravimetric

Calcium may be converted to carbonate, sulphate or fluoride and so w
The oxide above obtained may be converted to sulphate by moisteni
a few drops of water and then adding a slight excess of sulphuric acid
dilute). The excess sulphuric acid is driven off by heating over a lo
to SO_3 fumes and then more strongly at dull red heat until the excess
been expelled. A ring burner reduces the risk of spurting. Addition o
or so of ammonia to the cooled residue and reheating assists expulsio
acid. The residue is weighed as $CaSO_4$.

$CaSO_4 \times 0.2943 = Ca$ or $\times 0.4119 = CaO$ or $\times 0.7352 = CaCO_3$.

VOLUMETRIC DETERMINATION OF CALCIUM

Titration of the Oxalate with Permanganate [1]

This procedure may be applied successfully in a great variety of i
on account of the readiness with which calcium oxalate may be s
In the presence of iron, alumina, manganese, magnesia, etc., it is adv
make a reprecipitation of calcium oxalate to free it from adhering contam

The following reaction takes place when potassium permanganate
to calcium oxalate in acid solution:

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8$$

Procedure. Calcium oxalate, obtained pure, by precipitation and
according to directions given under the gravimetric determination of
is washed into a flask through a perforation made in the filter paper,
is treated with a little warm, dilute sulphuric acid [2] and the adherin
dissolved and washed into the flask. About 25 cc. of dilute sulphu
1 : 1, is added and the solution diluted to 250 to 300 cc.

When the precipitate has dissolved, the solution warmed to 60 c
is titrated with standard potassium permanganate, added cautiously
burette with constant agitation, until a faint permanent pink color is ob

One cc. N/10 $KMnO_4 = 0.0020$ gram Ca,[3] or $\times 0.0028 = CaO$.

Factors. $Ca \times 1.3993 = CaO$ or $\times 2.4974 = CaCO_3$ or $\times 3.3975 = C$
$\times 2.581 = Ca_3(PO_4)_2$.

Analysis of Limestone and Cement. See chapter on Cement by R
Meade.

[1] Fresenius, Hempel, Mohr, Sutton and others have testified to the
of this method for the determination of calcium.

[2] HCl in moderate quantity may be used in place of sulphuric acid witho
of liberating free chlorine as is the case in presence of iron.—Fleischer.

[3] From the reaction $2KMnO_4$, equivalent to 5O or 10H, reacts with
and $5Ca = (5 \times 40) \div 10 = 20$. A normal solution of calcium = 20 grams Ca
One cc. N/10 solution = 0.002 gram Ca.

CARBON

WILFRED W. SCOTT.

C,[1] *at.wt.* 12.0; *sp.gr. amorp.* 1.75–2.10; *cryst.: graphite,* 2.25; *diamond,* 3.47–3.5585; *m.p. sublimes at* 3500° C.; *oxides,* CO *and* CO_2

DETECTION[2]

Element. Carbon is recognized by its appearance and by its inertness towards general reagents. It is seen in the charring of organic matter when heated or when acted upon by hot concentrated sulphuric acid.

Upon combustion with oxygen or by oxidation with chromic and sulphuric acids, carbon dioxide is formed. The gas passed into lime water forms a white precipitate, $CaCO_3$. White precipitates are formed when the gas is led into baryta water ($BaCO_3$ ppt.), or into an ammoniacal solution of lead acetate ($PbCO_3$ pptd.).

Carbon Dioxide. Carbonates. CO_2 in Gas. A white precipitate with lime water, baryta water, ammoniacal solutions of calcium, or barium chlorides, or lead acetate (basic).

Carbonates. Action of mineral acids cause effervescence, CO_2 being evolved. The gas is odorless (distinction from SO_2, H_2S, and N_2O_3) and is colorless (distinction from N_2O_3). The gas absorbed in the reagents above mentioned produces a white precipitate. The test is best made by placing the powdered material in a large test-tube with a stopper carrying a funnel and delivery tube as shown in the illustration, Fig. 9. For small amounts of combined CO_2, warming of the test-tube may be necessary. Sulphuric or phosphoric acid should be used to liberate the gas, which is conducted into the reagent used for the test.

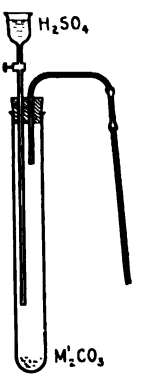

FIG. 9.—Test for Carbonate.

Distinction between Soluble Carbonates and Bicarbonates. The solution of the former is alkaline to phenolphthalein indicator (pink). Bicarbonate solutions remain colorless with this indicator. Normal carbonates precipitate magnesium carbonate when added to magnesium sulphate solution; bicarbonates cause no precipitation.

Free Carbonic Acid in Water in Presence of Bicarbonates. 0.5 cc. of rosolic acid (1 part acid in 500 parts of 80% alcohol), produces a red color with bicarbonates in absence of free CO_2, and a colorless or faintly yellow solution when free CO_2 is present.

Carbon Monoxide. The gas burns with a pale blue flame and is not absorbed by potassium hydroxide or lime water (distinction from CO_2). It is oxidized to CO_2 and so detected. With hot, concentrated potassium hydroxide, potassium formate is produced.

The gas is detected in the blood by means of the absorption spectrum.

[1] Van Nostrand's Chemical Annual, Olsen.
[2] Prescott and Johnson, "Qual. Chem. Anal."

ESTIMATION

The element occurs free in nature in the crystalline forms, diamond and graphite, and in the amorphous form, charcoal, coke, etc. It occurs in iron, steel, and in certain alloys. Its estimation in these metals is generally required. Carbon is determined in the analysis of organic compounds in which it is invariably combined and may also be present as free carbon (asphaltum).

Combined as a carbonate it occurs in a large number of substances, among which are found calcite, marble, limestone, dolomite, magnesite, strontianite, witherite, spatic iron ore. It occurs as the dioxide in the air, in water ($H_2O \cdot CO_2$) and in flue gas. Carbon dioxide is the active constituent of baking powders ($NaHCO_3$).

Preparation of the Sample

Iron, Steel, and Alloys. Drillings taken from different sections of the representative bar should be free from grease and dust. These are best kept in glass-stoppered bottles. Where a large number of daily samples are determined, it is found more convenient to use small manila envelopes, upon which the record of the analysis may be placed. Should it be impossible to obtain drillings free from grease, this impurity may be removed by heating the sample in an atmosphere of nitrogen, or by repeated extraction with ether.

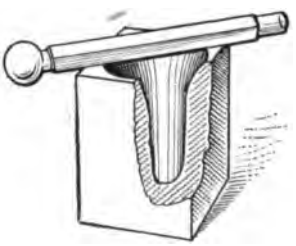

FIG. 10.—Chilled Steel Mortar.

Coarse chips, cast-iron drillings, etc., should be broken down in a chilled-steel mortar, Fig. 10. Carbon may now be separated in a definite weight of the sample as directed below, or it may be determined by direct combustion or by oxidation with chromic acid according to a procedure given later.

Organic Matter. It is advisable to fuse this in a nickel or iron crucible with sodium peroxide. The carbonate thus formed may be determined as usual. The organic substance may be oxidized directly in the combustion furnace.

Carbonates. Limestone, Dolomite, Cement, Alkali Carbonates and Bicarbonates. The powdered material is decomposed by addition of an acid as directed in the methods given later.

Separation of Carbon from Other Substances

The element is generally determined as carbon dioxide, in which form it is liberated from most of the combinations in which it occurs, free from other substances by ignition in a current of oxygen, or by oxidation with chromic acid as directed later.

Separation of Carbon in Iron and Steel. Cupric Potassium Chloride Method. 0.5 to 2 grams of the drillings are treated with 100 to 200 cc. of cupric potassium chloride solution and 10 cc. of hydrochloric acid (1.19). This mixture dissolves the iron according to the reaction

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2 + \text{carbon as a residue.}$$

The solution should be stirred frequently to hasten the solution of the iron. It is advisable to keep the temperature of the solution at about 50° C. When the iron and copper have dissolved the carbon is filtered off into a perforated platinum boat or crucible, as directed under the methods. It is now oxidized to CO_2 and so determined.

NOTE. The cupric potassium chloride solution is prepared by dissolving 150 parts of potassium chloride and 170 parts of crystallized cupric chloride in water and crystallizing out the double salt. Three hundred grams of this salt are dissolved in 1000 cc. The solution may be used several times by chlorinating the dirty brown filtrate from the carbonaceous residue. The cuprous chloride formed during the solution of the steel is converted again to cupric chloride, and the chlorinated double salt is even more energetic in its solvent action than the freshly made reagent. (Blair.)

GRAVIMETRIC METHODS FOR DETERMINATION OF CARBON

The determination of carbon by combustion with oxygen is made in two general classes of substances: *A*. Steel, iron and in certain alloys. *B*. Organic compounds. Carbon in steel and alloys is considered in two forms: carbide or combined carbon, and graphitic carbon. In organic substances carbon occurs principally combined with hydrogen, oxygen, and nitrogen. For the present we will consider procedures for the determination of carbon in steel and alloys.

The most accurate procedure for determination of carbon in steel, alloys, and in other materials containing the substance combined or free is by combustion with oxygen in a furnace heated by gas or electricity; the carbon dioxide formed being absorbed in caustic, and weighed.

Apparatus. Combustion Furnace. Although the gas furnace has been used more commonly on account of gas being more available than electricity, the extension of generating electric plants makes it possible to use electric furnaces, and these are gradually displacing those heated by gas, as they are more compact, easily manipulated and comparatively simple in structure.

A simple electric furnace may be made by wrapping a silica tube with a thin covering of asbestos paper, which has been moistened with water. On drying the paper will cling to the tube. A spiral coil of nichrome wire (Driver and Harris) is wound around this core. On a 2-foot length of tube two 45-foot lengths of No. 18 wire, connected in parallel, will heat the tube to bright redness, attaching the terminals to an ordinary light socket. The coils should be covered with ¼-in. coating of alundum cement. For appearance' sake as well as for protection, the tube is placed in a large cylinder of sheet iron, packed around with asbestos, and is held in position by circular asbestos boards placed at the ends of the large cylinder. The cylinder is mounted on a stand.

Absorption Apparatus. A large number of forms are for sale. The Geissler and Liebig bulbs have been popular (Figs. 11 and 12), but are now being displaced by forms that have less surface exposed, that are more easily cleaned and less fragile, such as Gerhardt's, Vanier's and Fleming's apparatus (Figs. 13, 14 and 16). The Vanier and the Fleming absorption apparatus are especially to be recommended, on account of their capacity, compactness, efficiency, in handling gases passing at a rapid rate, and their simplicity of form.

Procedure for Determining Carbon by Combustion. Mr. William R. Fleming [1] describes his apparatus in the Iron Age, Jan. 1, 1914. The following abstract is taken from Eimer & Amend's circular, edited by Mr. Fleming.

The greatest value of this rapid method is realized when it is used to follow a bath of steel in the open-hearth furnace preliminary to tapping. It abolishes

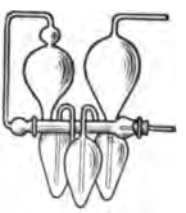

FIG. 11.—Geissler Bulb.

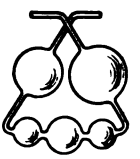

FIG. 12.—Liebig Bulb.

FIG. 13.—Gerhardt Bulb.

completely the unreliable and dangerous color carbon. By this method absolutely accurate results can be reported to the open hearth ten minutes after the drillings are received.

In principle this method is not new; in manipulation it is new. Heretofore chemists have been laboring under the impression that the flow of gas during a combustion must not exceed a certain snail-like pace. This false impression has been injected into the minds of chemists by a few who were supposed to have investigated the matter. The truth is that the faster oxygen is fed to burning steel the more complete the combustion will be. The rate of current is limited by the efficiency of the apparatus used to absorb the evolved carbon dioxide.

FIG. 14.—Vanier Bottle.

The Apparatus Described. The combustion train is shown complete in Fig. 15. The oxygen is delivered to the train through a regulating and reducing valve such as is used for welding. The regulating valve is not essential, yet any chemist who uses one will appreciate its convenience, especially in this method. Its convenience will be explained later. *K* is a mercury pressure gauge. It serves as a guide during the combustion and is an essential piece of apparatus. The graduated column is 6 ins. high and is divided into eighths. *P* is a washing bottle containing caustic potash solution. Filled to the mark indicated with 50% solution it will serve for at least 1000 combustions. It is used solely to indicate the flow of gas, not to purify it. If the chemist desires he may omit this from the train. *T* is a calcium chloride jar. It is filled to the mark indicated with finely divided calcium chloride, about pea size, retaining all the dust. A layer of asbestos is formed over the chloride and the remaining space filled with soda lime. The glass tubing leading from the jar is loosely packed for a distance of several inches with asbestos. This prevents any soda lime dust being carried into the combustion tube. *G* is a mercury valve like that used in Johnson's train. It is used solely to maintain an atmosphere of

[1] Metallurgist, Andrews Steel Company, Newport, Ky.

pure oxygen in the purifying train, a condition essential to accurate results. It is not used to prevent carbon dioxide backing into the purifying train, of which there is not the remotest possibility.

The combustion tube is the ordinary fused silica tube glazed on the inside only. The tube is 30 ins. long with inside diameter of from $\frac{7}{8}$ to 1 in. One tube of 30 ins. will serve twice as long as one of 24 ins. It is loosely packed with asbestos for a distance of 6 ins. at the exit end, and 3 ins. is allowed to project from the furnace. For about the first 100 combustions, the combustion boat is pushed close against the asbestos. The portion of the tube immediately above this will become coated with iron oxide. The asbestos is then moved up so that it covers this portion of the tube and a fresh area exposed to the spraying oxide. In this manner one tube can be made to serve 600 combustions or even more. Both platinum and nickel cylinders have been used inside the tube to protect it from the spraying oxide, but it is doubtful whether this practice pays. These cylinders are not used in this laboratory because it is believed that they delay incipient combustion for at least thirty seconds.

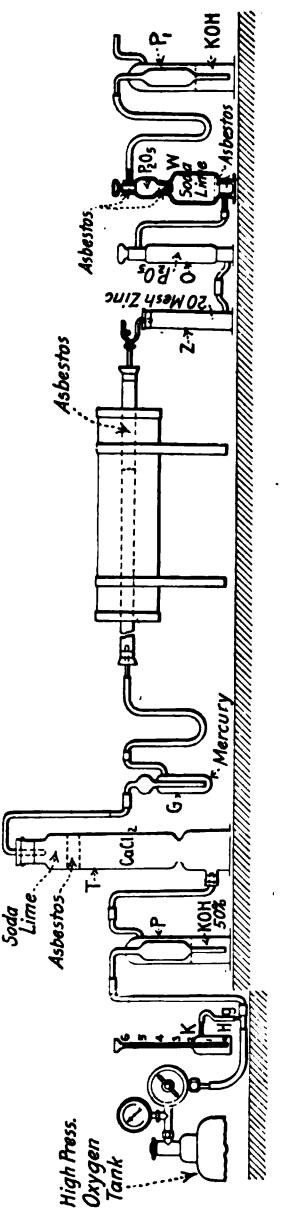

FIG. 15.—Fleming's Apparatus for Determination of Carbon by Combustion.

The Furnace and Combustion Tube. The furnace used is one of the ordinary resistance type. It is constantly maintained at a temperature of 1000° C. This temperature is verified daily by the use of a pyrometer. Many claim to be expert at judging temperatures, but none are expert enough to be without a pyrometer. The two-way stop following the combustion tube will be found very convenient when it is not desirable to pass the current through the jars *Z* and *O*.

Z is filled with 20-mesh zinc. Once filled it will serve for several thousand combustions. As a matter of fact it is included in this train as a filter. If nickel boats and aluminum are used the chemist may omit this zinc jar from the train, for with all ordinary grades of steel it serves no purpose.

O is the phosphoric anhydride jar. A little asbestos is placed in the lower part just above the lower stopper. The remaining space in the jar is completely filled with phosphoric anhydride. The upper stopper is packed tightly enough to prevent any powder being swept into the weighing apparatus. As the anhydride liquefies it passes down into the lower stopper, where it can be removed conveniently without disturbing the anhydride above it. Likewise

the anhydride can be replenished by removing only the upper stopper. The jar need not be washed oftener than once in 500 combustions. When filled with anhydride, fresh reagent need not be added for at least 150 combustions. After each combustion the jar should be given a few sharp taps with the hand to prevent canals being formed.

Details of the Absorption Apparatus. The absorption apparatus, shown in detail in Fig. 16, has been modified slightly at the suggestion of Henry G. Martin, of the Railway Steel Spring Company, Chicago Heights, Ill. This apparatus is no more efficient than the old style, but it is much more convenient and less troublesome. In the old-style tube the anhydride would liquefy after several days and require replenishing. To overcome this, Mr. Martin suggested using separate chambers for the anhydride and soda lime, so that communication could be broken when the tube was standing idle. The tube shown, Fig. 16, is Fleming's modification of Mr. Martin's suggestion. When properly filled this tube will serve for at least 70 combustions when operating on 1.5 grams of sample containing 1.03% carbon.

FIG. 16.—Fleming Absorption Apparatus.

The anhydride in the upper chamber serves for at least 300 combustions. Soda lime, placed in the lower tube in alternate layers ($\frac{1}{8}$ in.) of the different meshes, has proven a very convenient and desirable reagent. The 12-mesh soda lime for nitrogen can also be used with excellent results. If this is employed, part of it should be ground to about 60-mesh and alternate layers of fine and coarse used.

It is exceedingly important that the tube be loaded with alternate layers of coarse and fine reagent, for, if the 12-mesh reagent is transferred directly from the bottle to the absorption tube, the latter will fail to be effective for more than 30 combustions and in some cases less. The reason for this is evident. The lower stopper is packed loosely with asbestos, also the lower portion of the soda lime chamber just above the stopper. Beginning with a layer of 12-mesh soda lime, the entire chamber is filled with alternate layers of fine and coarse reagent. The small diameter of the anhydride chamber is packed with asbestos and the remaining space filled with phosphoric anhydride. Finally, the upper stopper is packed with asbestos. The anhydride chamber, filled as indicated, will not require refilling for at least 300 combustions. It is not necessary to turn the chamber to break communication while the tubes are idle, for the packing of the small diameter with asbestos prevents the absorption of moisture from the soda lime. The tubes must be used in pairs, so that one serves as a tare in weighing the other. A pair of tubes assures the operator of at least 140 combustions. A glass or rubber tubing about 12 ins. long serves as a guard for the absorption tube. It connects the bottle, P_1, which is used to indicate flow of gas.

The use of clay boats has been abandoned in favor of nickel boats filled with alundum. These are greatly superior to clay boats in every conceivable way. The alundum is labeled as being free from carbon, but this is not true. In fa some of it contains considerable carbon. It should always be burned in oxy at 1000° before using. The boats are formed out of 22-gauge pure sheet nick One boat will serve for about 100 to 150 combustions, some more, some less.

Details of the Analysis. The furnace being at 1000°, the two freshly prepared absorption tubes are placed in the train and oxygen run through at the rate of 300 cc. per minute for fifteen minutes. This insures the displacement of all air from the purifying train as well as the absorption tubes. Remove one absorption tube from the train and turn on the oxygen until the mercury stands at about 2 ins. The rate of current is then measured by inverting a graduated cylinder filled with water. Several trials will establish a rate of about 325 cc. per minute. Note the reading of the column of mercury at this rate and subsequently, when using the same absorption tube, maintain this same pressure in the train and the rate of flow will be 325 cc., the rate during all combustions. Shut off the oxygen and, when it comes to a slow bubbling through P_1, close the upper stopper of the absorption tube. Disconnect it from the train, but do not close the lower stopper for about five seconds after disconnection. Weigh against its mate as a tare. It is now ready for the first combustion.

Weigh 1.5 grams of drillings, preferably thin, curly drillings from a twist drill, and spread out in the nickel boat which is half filled with alundum. Place the absorption tube in the train and place its mate beside it. With the oxygen flowing about 100 cc. per minute, the drillings are pushed into the combustion tube. The current is immediately run up to the desired pressure, which gives 325 cc. per minute. The regulator will do the rest. It will feed the oxygen automatically to the burning steel. As a rule the drillings are entirely burned one and one-half minutes after insertion. Continue the flow of oxygen for three and one-half minutes more (five minutes, total time) and disconnect as before the absorption tube. Weigh immediately. The result will be accurate and reliable. Whether determining carbon in a standard steel, where the greatest accuracy is required, or in a bath test, the time required is always five minutes.

The weight of the boat, plus refractory lining, should be kept as low as possible, so as not to introduce too much cold material into the combustion tube. The boats used in this laboratory are ½ in. wide, ¼ in. deep and 3 ins. long. Sheet nickel varies in percentage of carbon. As a rule, a nickel boat must be ignited in oxygen at 1000° for one to two hours.

There seems to be a difference of opinion concerning the physical condition of the steel after burning, some chemists believing that inaccurate results are obtained if the drillings have fused during combustion. Others maintain that complete fusion of the drillings is essential to accurate result. If drillings which happen to be a little thick are used, low results are obtained unless these are *perfectly fused.*

Graphitic Carbon

In Iron and Steel. The sample of 1 gram of pig iron or 10 grams of steel is treated with 15 cc. of nitric acid (sp.gr. 1.2), per gram of sample taken. When all the iron has dissolved, the graphite is allowed to settle and the supernatant liquid decanted onto an ignited asbestos filter, using either a perforated boat, Fig. 17, or a filtering tube. The residue is transferred to the filter, and washed thoroughly with hot water. It is treated with hot caustic solution (sp.gr., 1.1), washed thoroughly again with hot water, then with a little dilute hydrochloric acid, and finally with hot water. The carbon is now burned by one of the procedures given—the oxidation in the combustion

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furnace being recommended. The CO_2 is absorbed in caustic and estimated according to the standard procedure given for carbon.

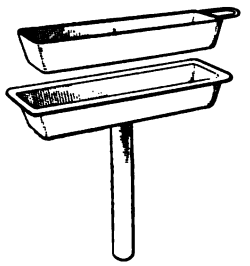

FIG. 17.—Boat and Holder for Carbon Determination.

$$CO_2 \times 0.2727 = \text{graphitic carbon.}$$

The perforated boat, shown in the cut, fits snugly into the receptacle below. Sufficient asbestos is poured into the boat to form a film over the bottom. A seal is made around the boat with additional asbestos, the apparatus having been inserted in a rubber stopper in the neck of a suction flask and suction applied.

The apparatus is recommended by Blair for combustion of graphitic carbon or of total carbon liberated from iron or steel by the cupric potassium chloride method. The boat may be placed directly in the combustion tube and the carbon oxidized as usual.

The Shimer Combustion Apparatus[1]

The apparatus, designed for the rapid determination of iron and steel, is in general applicable to the same class of chemical operations as is the combustion tube of platinum, silica, or porcelain. It offers the advantage of neatness, reduction in the number of parts to be handled, diminished consumption of gas, and increased ease of manipulation. The simplified form, shown in the cut, Fig. 18, enables the use of the standard form of platinum crucible, *A*, with its inner wall ground to fit a tapered nickel, water-jacketed stopper, *B*. The rubber jacket of the original type is eliminated and a detachable nickel reinforcing ring, *C*, at the top of the crucible serves the double purpose of completing the security of the seal and as a support for the apparatus.

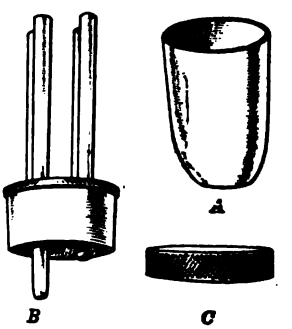

FIG. 18.—Shimer Combustion Apparatus, Simplified Form.

Water is circulated through the stopper through the tubes *C* and *D*. The current of oxygen passes through *A* into the crucible, oxidizing the material within the crucible, which is heated to red heat with a burner placed below it. The carbon dioxide formed passes through *B* to the absorption train. The remainder of the apparatus for the determination is the same as is used with the combustion tube. An asbestos shield protects the upper portion of the outfit, the crucible fitting snugly in a hole in the asbestos board.

Combined Carbon

Indirect Method. The excess of carbon remaining when the graphitic carbon is subtracted from total carbon (in iron and steel), is calculated as combined carbon. This difference method is generally accepted as being the most accurate for estimation of combined carbon.

[1] Courtesy of Baker Platinum Works.

NOTES. In chromium, tungsten and titanium steels a temperature of 1500° C. is necessary to oxidize the carbon by direct combustion for thirty minutes. (J. R. Cain and H. E. Cleaves, J. Wash. Acad. Sci., 194, 4, 393–397.)

Carbon in Soils. One to 3 grams of 60-mesh sample is treated with a solution of 3.3 grams CrO_3+10 cc. H_2O and 50 cc. conc. H_2SO_4 (1.84). The evolved CO_2 is absorbed in standard caustic and titrated with acid, phenolphthalein and methyl orange being used as indicators. (J. Ind. Eng. Chem., 1914, 6, 843–846.)

DETERMINATION OF CARBON IN ORGANIC SUBSTANCES

Combustion of Organic Substances Free of Nitrogen, Halogens, Sulphur, and the Metals

The following modification of the procedure described for determination of carbon in iron and steel is applicable to the determination of carbon in organic substances free from the substances mentioned above.

Apparatus. This is practically the same as that shown in Fig. 19, with the exceptions that copper plugs may be used to advantage in place of the platinum plugs. In the absorption end of the train a calcium chloride tube is preferred. The calcium chloride should have been saturated with dry CO_2 gas, the excess of which has been removed by a current of pure air. This tube

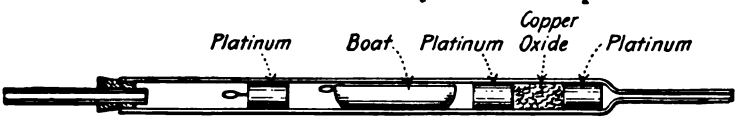

FIG. 19.—Diagrammatic Sketch of Combustion Tube.

is weighed as well as the potash bulb, the calcium chloride retaining the water formed by the combustion of the hydrogen of the organic substance, which is thus determined.

The organic substance, if a solid, is introduced into the combustion boat directly; if it is a liquid, it is held in a bulb blown in a capillary tube. One end of the tube is sealed and a bulb blown. When cool, the tube is weighed, and the material then introduced by first warming the bulb and then inserting the open end of the tube into the liquid to be examined. By cooling the bulb, liquid is drawn into the tube. The end is wiped off, and the liquid expelled from the capillary by gently heating this portion. The end is now sealed if the liquid is volatile, otherwise it is left open, and the tube is weighed. The increased weight is due to the organic substance. The tip of the capillary is now broken, if sealing was necessary, by means of a file. The tube containing the sample is placed in the boat, the open end of the capillary pointing toward the open end of the combustion tube. After connecting up the apparatus, the copper oxide end of the tube is heated to redness and oxygen slowly passed through the tube at such a rate that the bubbles in the potash bulb can be readily counted. The entire tube is now heated and remaining operation is the same as has been described for iron and steel combustion.

The gain of weight of the calcium chloride tube is due to water formed by the combustion of hydrogen of the compound, that of the potash bulb to the carbon.

$$H_2O \times 0.1121 = H,$$
$$CO_2 \times 0.2727 = C.$$

NOTE. The oxygen gas should be free from hydrogen. A preheater, before the purifying tubes of the train, causes the combustion of the hydroge the absorption of the water formed before the gas enters the combustion tube.

Determination of Carbon and Hydrogen in Nitrogenous Substances

A modification of the first procedure described for determinations of c and hydrogen in organic substances must be made, since from subs containing nitrogen, nitroso and nitro compounds, oxides of nitrogen are f which would be absorbed in the calcium chloride and potash bulbs, giving results for hydrogen and carbon. To overcome this difficulty, a copper that has been reduced (See note below) is placed in the front end combustion tube (to the right in Fig. 19) to reduce the oxides of nitro nitrogen.

NOTE. Reduction of copper spiral may be accomplished as follows: The spiral is prepared by rolling together a piece of copper gauze about 10 centi wide, making it as large as will conveniently pass into the combustion tube spiral is heated till it glows by holding it in a large gas flame, and whi hot it is dropped into a test-tube containing 1 or 2 cc. of methyl alcohol or This quickly boils away, igniting at the end of the tube. The copper is com reduced to bright metallic copper. The spiral is taken out with a pair of c tongs and dried by quickly passing it through a flame a few times, and whi still warm it is introduced into the front of the combustion tube.[1]

The substance is introduced into the tube and the connections made. copper oxide spiral, that was pushed after the boat, is heated, and th reduced spiral (right end of tube). The oxide near the boat, and the entire tube is heated to a red heat. When the bubbles cease to s the potash bulb, the stopcock is opened to the oxygen-purifying train slow flow of oxygen turned on, the gas allowed to pass through the tub it can be detected with a glowing splinter at the exit of the absorption the apparatus.

If the substance is difficult to burn, it is mixed with freshly ignited copper oxide, which assists combustion.

The remainder of the operation is the same as has been described.

Organic Substances Containing Halogens

The procedure is the same as that described for nitrogenous subs with the exception that a silver spiral is used in place of the reduced spiral. The heating of this spiral should be between 180 and 200° C over 200°).

Organic Substances Containing Sulphur

These are best ignited with sodium peroxide and the carbonate for determined by the procedure given for carbon dioxide in carbonates.

The Wet Combustion Process for Determination of Carb

The method depends upon the oxidation of carbon to carbon dioxid the powdered material is digested with a mixture of concentrated su acid and chromic acid, or potassium dichromate, or permanganate. T

[1] Treadwell and Hall, "Quantitative Analysis." John Wiley & Sons.

cedure is applicable to oxidation of free carbon, carbon combined in organic substances and in certain instances to carbon combined with metals, where the substance may be decomposed by the action of the acids.[1] It is of value in determination of carbonates in presence of sulphides, sulphites, thiosulphates and nitrites, which would vitiate results were they not oxidized to more stable forms, from passing into the potash bulb with the carbon dioxide.

Apparatus. The apparatus is identical with that used for determining carbon dioxide in carbonates, Fig. 20, with the exception that in place of the acid bulb nearest the decomposition flask two bulbs are placed. The first of these contains a strong solution of chromic and sulphuric acids, the second is filled with glass beads moistened with chromic acid solution. Following this is the drying bulb containing concentrated sulphuric acid and finally the absorption apparatus, as shown in the illustration.

Procedure. 0.2 to 1 gram of the powdered material, fine drillings, free carbon, or organic substance is placed in the decomposition flask. If the material is apt to pack it is advisable to mix with it pure ignited sea-sand to prevent this. Five to 10 grams of granular potassium dichromate are added and the apparatus swept free of carbon dioxide by passing purified air through it before attaching the absorption apparatus. The potash bulb is now weighed, using a counterbalance bulb and following the precautions given in the dry-combustion method. The bulb is attached to the train.

Oxidation. Concentrated sulphuric acid placed in the acid funnel, attached to the decomposition flask, is allowed to flow down on the sample until the funnel is almost empty; the stop-cock is then closed. A flame is placed under the flask, when the vigorous action has ceased, and the material gently heated until the reaction is complete and the organic matter or carbon completely oxidized.

The apparatus is now swept free of residual CO_2 by applying suction, the gas being completely absorbed by the potash, or the soda lime reagent.

The increase of weight of the absorption bulb is due to carbon dioxide.

$$CO_2 \times 0.2727 = C.$$

NOTE. The following additional purifiers are frequently advisable: (*a*) an absorption bulb containing silver sulphate to absorb chlorine and vapors from sulphur compounds; (*b*) a capillary tube of silica or platinum heated to a dull redness to oxidize any hydrocarbons, carbon monoxide, etc., that may be evolved and imperfectly oxidized by the chromic acid.

DETERMINATION OF CARBON DIOXIDE IN CARBONATES

The method is applicable for determination of carbon dioxide in limestone, dolomite, magnesite, strontianite, witherite, spatic iron ore, carbonates of sodium, and potassium, bicarbonates in baking powder, carbon in materials readily oxidized to CO_2 chromic sulphuric acid mixture. The procedure depends upon the evolution of carbon dioxide by a less volatile acid, or the oxidation of carbon. The CO_2 is absorbed in caustic and weighed.

Apparatus. The illustration shows the apparatus found suitable for this determination. It is Knorr's apparatus slightly modified. The absorption bulb or bottle should be one that will effectively absorb carbon dioxide entering

[1] Not applicable for determining carbon in ferro-silicon, ferro-chrome or tungsten steel.

at a rapid rate. The Vanier or the Fleming forms is satisfactory for purpose.

Procedure. A sample weighing 0.5 to 2 grams, according to the ca dioxide content, is placed in the dry decomposition flask (*C*). The flas closed by inserting the funnel tube (*B*) fitted with the soda lime tube (*A*), connected by means of a condenser to the train for removing impurities f carbon dioxide, leading to the absorption bulb, as shown in Fig. 20.

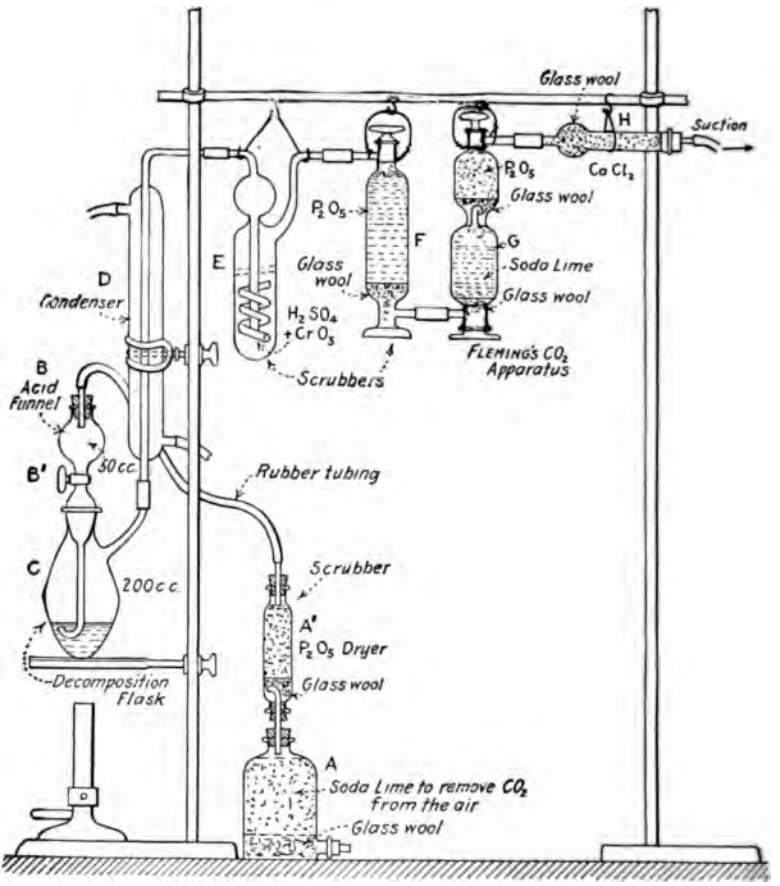

FIG. 20.—Apparatus for Determining Carbon Dioxide.

The apparatus is swept out with a current of dry, purified air before attac the weighed absorption bottle. This is accomplished by applying gentle suc at the end of the purifying train. The absorption apparatus is now atta (Fleming absorption apparatus is shown in the illustration). The tube is nearly filled with dilute sulphuric acid (1 : 3), the stop-cock (*B'*) being cl The soda lime tube is now inserted into place as shown in the cut. The in (*B*) is now allowed to run slowly down on the sample at a rate that ev

gas not too rapidly to be absorbed; 1 to 2 cc. of acid being retained in (*B*) to act as a seal, the stop-cock (*B'*) being then closed.

When the violent action has ceased, the solution in (*C*) is heated to boiling and boiled for about three minutes. If the sample is baking powder, or contains organic matter, the decomposition flask is protected from excessive heat by placing a casserole of hot water under it. This prevents charring of the starch or organic matter, which would be apt to occur if the direct flame was used. Gentle suction is now applied to the absorption end of the apparatus and the stop-cock (*B'*) opened, allowing the remainder of the acid to flow into the flask (*C*) and admitting a current of air, purified by passing through the soda lime in (*A*). The suction should be gentle at first, and then the speed of the flow increased to the full capacity of the absorption bottle. A fairly rapid current is preferred to the old-time procedure of bubbling the gas through the apparatus at a snail-like pace, but discretion should be used in avoiding a too rapid flow.

In the analysis of baking powders, where foaming is apt to occur, the decomposition flask should be of sufficient capacity to prevent foaming over. A small flask is generally to be preferred for obvious reasons. By gently heating to boiling during the passage of the air, steam assists in expelling any residual CO_2 in the flask. When the passage of air is rapid, this boiling should be discontinued.

The increase of weight of the absorption bottle is due to the carbon dioxide of the sample. This procedure gives total CO_2.

Determination of Carbon Dioxide by Measuring the Gas

Fairly accurate results may be obtained by measuring the gas evolved. A large cylindrical tube having a capacity of about 1100 cc. is used. The tube is graduated from 1000 cc. to 0 at the upper portion of the cylinder; a space of about 100 cc. remains at the upper portion. A tube extending from a little above the 0 graduation to the bottom of the cylinder carries out the water as the gas is admitted.

To make the run, the cylinder is filled to the mark 0 with saturated salt solution.[1] It is now connected to a condenser.[2] Twenty-five cc. of saturated salt solution are admitted to the decomposition flask, and the generated gas measured by the water displacement in the tube described. Calculations are made after reduction to standard conditions. 5.1 cc. CO_2 at 0° C. and 760 mm. weigh 0.01 gram.

Residual Carbon Dioxide

This is the CO_2 remaining after baking powder has been treated with water and the evolved CO_2 expelled by warming.

The procedure recommended by the U. S. Department of Agriculture is as follows:[3]

[1] H. W. Brubacker, Jour. Ind. Eng. Chem., 1915, 7, 432.

[2] The nitrometer may be used in place of the cylinder and atmospheric conditions obtained as usual. Formula for reduction to 760 millimeters and 0° C.:

$$V' = V \frac{(P-w)}{760(1+.00367t)}.$$

[3] Bureau of Chem. Bulletin No. 107.

Weigh 2 grams of baking powder into a flask suitable for the subsequent determination of carbonic acid, add 20 cc. of cold water, and allow to stand twenty minutes. Place the flask in a metal drying cell surrounded by boiling water and heat, with occasional shaking, for twenty minutes.

To complete the reaction and drive off the last traces of gas from the semi-solid mass, heat quickly to boiling and boil for one minute. Aspirate until the air in the flask is thoroughly changed, and determine the residual carbon dioxide by absorption, as described under total carbonic acid.

The process described, based on the methods of McGill and Catlin, imitates, as far as practicable, the conditions encountered in baking, but in such a manner that concordant results may be readily obtained on the same sample, and comparable results on different samples.

Available Carbon Dioxide

The residual is subtracted from the total, and the difference taken as available CO_2.

Determination of Carbon Dioxide by Loss of Weight

An approximate estimation of the carbon dioxide in carbonates—baking powders, bicarbonate of soda, limestone, etc., may be obtained by the loss of weight of the material when treated with a known weight of acid.

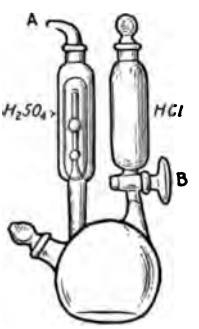

FIG. 21.—Schroetter's Alkalimeter.

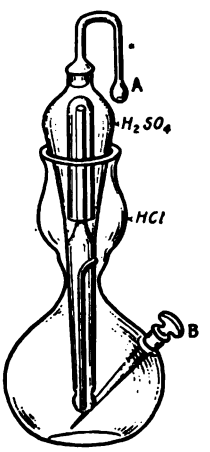

FIG. 22.—Mohr's Alkalimeter.

Various forms of apparatus are used for this determination. The Schroetter and Mohr types are shown, Figs. 21 and 22.

About 0.5 to 1.0 gram of sample is taken and placed in the bottom of the flask, dilute hydrochloric and strong sulphuric acids then placed in the bulbs as indicated in the illustrations. The apparatus is weighed as it is thus charged. The hydrochloric acid is now allowed to flow down on the carbonate and the stopper closed. The evolved gas passes through the strong sulphuric acid, which absorbs the moisture. After the vigorous action has subsided the appa-

ratus is placed over a low flame and the solution heated to boiling and boiled very gently for about three minutes. CO_2-free air is aspirated through the solution to expel the last traces of CO_2, by applying gentle suction at *a* and opening *b*, the air being purified by passing through soda lime. The apparatus is again weighed and the loss of weight taken as the CO_2 of the material.

Available CO_2 in baking powder may be determined by substituting water in place of hydrochloric acid.

VOLUMETRIC METHODS FOR THE DETERMINATION OF CARBON

Total Carbon. Absorption of Carbon Dioxide in Barium Hydroxide

The carbon dioxide evolved by oxidation of the material by dry combustion with oxygen or by oxidation with chromic sulphuric acid mixture is absorbed in barium hydroxide, free from carbonate, and the precipitated barium carbonate titrated with standard hydrochloric acid.

Procedure. The essential difference in this method from those already described under the gravimetric methods is in the fact that a perfectly clear saturated solution of barium hydroxide is used for absorption of the carbon dioxide in place of caustic potash. Considerable care must be exercised to prevent contaminating the reagent with carbonate. The solution is drawn by suction through a siphon, dipping below the surface of the reagent, into the absorption tube, which should be of such construction that the material may readily be poured out. After absorption of the CO_2 gas, the apparatus is disconnected and the excess barium hydroxide neutralized with dilute hydrochloric acid (1 : 4) using phenolphthalein indicator. A few drops of methyl orange are now added and a measured excess of standard hydrochloric acid run in from a burette. After heating to boiling the excess acid is titrated with standard caustic sclution, 1 cc. of which is equivalent to 1 cc. of the hydrochloric acid.

$$HCl \times 0.1646 = C.$$

1 cc. N/10 HCl = 0.0022 gram CO_2.

NOTE. The method is used in the Omaha laboratory of the Union Pacific Railroad. Dr. N. F. Harriman, Chief Chemist, informed the writer (W. W. Scott), that with care no difficulty is experienced with contamination of the barium hydroxide and excellent results are obtained. The Victor–Meyer bulb is used for holding the barium hydroxide.

Determination of Carbon by Measurement of the Volume of Carbon Dioxide Evolved by Oxidation of Carbon, or by the Decomposition of Carbonates with Acid.

Description of the Scheibler and Dietrich Process and that of Lunge and Marchlewski are given in Mellor's work on "Inorganic Analysis," pp. 555–559, 1st Ed. A modification of Wiborg's method is described in Blair, "Chemical Analysis of Iron," pp. 146–149, 7th Ed.

Determination of Carbon Dioxide in a Gas Mixture.

See Gas Analysis.

Direct Colorimetric Method for Determination of Combined Carbon

The procedure is of value to the steel laboratory where a large number of daily determinations of combined carbon are required. By this method over a hundred determinations a day may be made by an experienced manipulator. The method depends upon the color produced by combined carbon dissolved in nitric acid, the depth of color increasing with the combined carbon content of the material. Comparison is made with a standard sample of iron or steel, which is of the same kind and in the same physical condition as the material tested.[1] That is to say, a Bessemer steel should be compared with a Bessemer standard, open hearth with open hearth, crucible steel with crucible steel, the standards containing approximately the same amounts of carbon, and as nearly as possible the same chemical composition. The samples should be taken from the original bar which has not been reheated, hammered, or rolled. Copper,

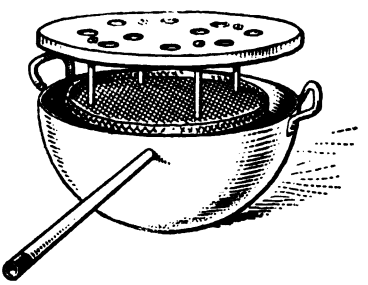

FIG. 23.
Hot Water Racks for Test Tubes.

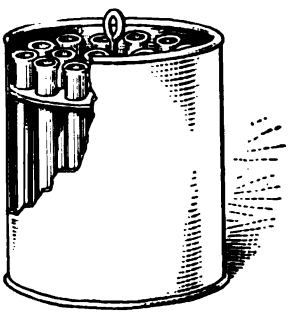

FIG. 24.
Color Carbon Determination.

cobalt, and chromium will interfere with the test; the other elements have very little effect.

Procedure. One standard sample of 0.2 gram and the same amount of sample drillings are taken for analysis. The weighings are conveniently made in brass or aluminum pans, boat-shaped to enable the drillings to be dumped into test-tubes. A counterpoise, weighing the same as the boat, is placed on the opposite pan, together with the 0.2 gram weight. A magnetized knife will assist in removing the excess of material. The weighed sample is brushed into a test-tube 6 ins. long (150 mm.) $\frac{5}{8}$ in. (16 mm.) in diameter. (Each test-tube has a label near the open end to distinguish the sample.) A rack or a 600-cc. beaker may be employed for holding the test-tubes during the weighing. After the batch is ready the tubes are transferred to a perforated rack (Figs. 23 or 24) and this then stood in the water bath filled with cold water.

The proper amount of nitric acid (sp.gr. 1.2; e.g., 1 conc. HNO_3 : 1 H_2O), from a burette, is now added to each test-tube.

3 cc. HNO_3 for 0.3% C.
4 cc. HNO_3 for 0.3 to 0.5%.
5 cc. HNO_3 for 0.5 to 0.8% C.
6 cc. HNO_3 for 0.8 to 1% C.
7 cc. HNO_3 for over 1% C. steel[1].

[1] Blair, "The Chemical Analysis of Iron."

The depth of color produced by the acid will give an idea of the amount required. One cc. of acid is added at a time until the depth of color is correct. This requires experience gained from observation of the color produced by standard samples. The acid is added slowly to the coarse drillings. Insufficient acid gives a darker tinted solution than it properly should be. The nitric acid should be free from chlorine and hydrochloric acid, since these produce a yellow color. (Cl and $FeCl_3$ are yellow.)

A glass bulb or a small funnel is placed in each test-tube and the water in the bath then heated to boiling and boiled until all the carbonaceous matter has dissolved, the tubes being shaken from time to time to prevent formation of a film of oxide. Low-carbon steels require about twenty minutes, whereas steels of over 1% carbon require about forty-five minutes. (Blair.) As soon as the bubbles cease and the brownish flocculent matter disappears, the rack is removed from the bath and placed in a casserole of cold water. (Prolonged heating and strong light each causes fading of the color due to combined carbon.)

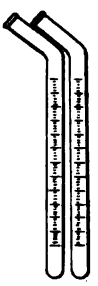

FIG. 25.—Carbon Tubes.

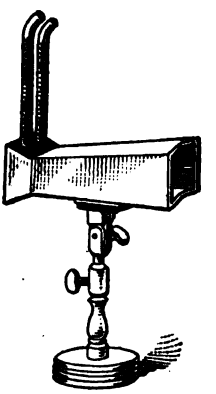

FIG. 26.—Color Comparator or Camera.

Color Comparison. This is made in graduated, clear, colorless, glass cylinders called carbon tubes. The form shown in Fig. 25 was found by the writer [1] to be the most satisfactory type for a steel-works laboratory where rapidity of manipulation was essential. The bend at the upper portion of the tube facilitates mixing of the solution upon dilution with water, the tube being tilted back and forth until the solution is homogeneous, the bend preventing the liquid from spilling. The dilution should be at least twice that of the amount of nitric acid used, as this amount of water is necessary to destroy the color due to ferric nitrate.

The standard is poured into the carbon tube and the rinsings from the test-tube added. The solution is diluted to a convenient multiple in cc. of the carbon content. For example, 0.45% carbon sample may be diluted to 9 cc., then each cc. will represent 0.05% carbon. The sample is placed in a second tube of exactly the same diameter, wall thickness, and form. If the solution of the sample is darker than the standard, water is added little by little,

[1] W. W. Scott.

followed by mixing, until the shade matches the standard. If the standard, on the other hand, is darker than the sample, a greater dilution of the standard is necessary, the cc. again representing a multiple of the carbon content. For example dilution of the .45% carbon sample to 15 cc. makes each cc. to represent 0.03 carbon. (It is frequently advisable to take a standard of lower carbon content in place of greater dilution of the standard.)

Example. Suppose in the first case the dilution of the sample was 15 cc. in order to match the standard, then $15 \times 0.05 = 0.75\%$ carbon. Six cc. dilution case $2 = 6 \times 0.03 = 0.18\%$ carbon.

The color comparison can be best made in a "camera," a long box with one end closed by a ground-glass screen, Fig. 26. Parallel to the screen and near it, two holes through the top of the box admit the test-tubes. The inner walls of the camera are blackened to prevent reflection of light. If a camera is not available, the tubes may be held side by side and compared against a sheet of white paper held as a background.

ANALYSIS OF GRAPHITE

Determination of Carbon

The procedure for determining carbon in graphite is the same as that described for determination of carbon in difficultly combustible organic substances.

The material is broken down in a steel mortar and powdered in an agate mortar. About 0.2 gram is taken for the determination and mixed with copper oxide to assist the combustion, then placed in the boat and the combustion of the carbon carried on according to the standard method in the combustion tube.

$$CO_2 \times 0.2727 = C.$$

VOLUMETRIC DETERMINATION OF HYDROCYANIC ACID[1]

The method depends upon the decolorization of the blue ammoniacal solutions of cupric salts by a soluble cyanide, the reduction to cuprous condition being available for an accurate quantitative estimation of the cyanide.

Standard Copper Sulphate. Twenty-five grams of copper sulphate, $CuSO_4 \cdot 5H_2O$ are dissolved in a 1000-cc. flask with 500 cc. of distilled water and ammonium hydroxide added until the precipitate that first forms dissolves and a deep blue solution is obtained. Water is now added to make the volume exactly 1000 cc. The cupric solution is standardized by running a portion into a solution containing 0.5 gram pure potassium cyanide, KCN, per 100 cc. of water and 5 cc. of ammonium hydroxide until a faint blue color is evident. Chlorides do not interfere.

Procedure. 0.5 gram of the soluble cyanide is dissolved in 100 cc. of water and 5 cc. strong ammonium hydroxide added. The standard cupric sulphate solution is now added until the blue color is obtained. The cc. required multiplied by the factor of the copper salt in terms of the salt sought gives the weight of that salt in the sample.

NOTE. Test for Cyanide. This depends upon the solvent action of HCN upon freshly precipitated HgO in presence of KOH. The filtrate is tested for mercury in an acid solution by addition of H_2S. (Hood.)

[1] J. McDowell, C. N., 1904, p. 221.

Liebig's Method for Determination of Hydrocyanic Acid. Soluble Cyanides[1]

Silver nitrate reacts with an alkali cyanide in neutral or alkaline solution as follows: $AgNO_3+2KCN=Ag(CN)_2K+KNO_3$. The potassium silver cyanide is soluble, hence the precipitate that first forms immediately dissolves on stirring as long as the cyanide is present in excess or in sufficient quantity to react according to the equation. A drop of the silver salt in excess will produce a permanent turbidity, owing to the following reaction:

$Ag(CN)_2K+AgNO_3=2AgCN+KNO_3$, the insoluble AgCN being formed.

Procedure. The alkali cyanide contained in a beaker placed over a sheet of black glazed paper, is treated with 4 to 5 cc. of 10% KOH solution and diluted to 100 cc. The liquid is now titrated with standard silver nitrate, with constant stirring, until a faint permanent turbidity is obtained.

One cc. N/10 $AgNO_3=0.0013022$ gram KCN.

For his review and criticism of this chapter the author wishes to mention Mr. J. M. Cratty, Chief Chemist, U. S. Navy Yards, Philadelphia, Pa.

[1] Ann. d. Chem. und Pharm., 77, p. 102.

CERIUM AND THE OTHER RARE EARTHS

R. STUART OWENS [1]

Group.*	Symbol.	At. Wt.†	Sp. Gr.	M. P.	Oxides.
Yttrium	Yt	88.7	3.800	1250	Yt_2O_3
Erbium	Er	167.7	4.770	.....	Er_2O_3, Er_4O_7
Holmium	Ho	163.5			
Thulium	Tm	168.5	.....	.....	Tm_2O_3
Dysprosium	Dy	162.5			
Ytterbium (Neo-ytterbium)	Yb	173.5	.....	1800	Yb_2O_3
Lutecium	Lu	175.0			
Europium	Eu	152.0			
Victorium		Discovery	not confirmed.		
Group 2:					
Terbium	Tb	159.2	.....	.....	Tb_2O_3
Gadolinium	Gd	157.3	1.310	.....	Gd_2O_3
Group 3:					
Cerium	Ce	140.25	6.625	950	Ce_2O_3, Ce_2O_5
Lanthanum	La	139.0	6.163	.....	La_2O_3
Neodymium	Nd	144.3	6.544	840	Nd_2O_3
Praseodymium	Pr	140.9	6.544	940	Pr_2O_3
Samarium	Sa	150.4	7.700	1350	Sm_2O_3
Scandium	Sc	44.1	.....	1300	Sc_2O_3
Decipium		Discovery	not confirmed.		

* According to Böhm (Browning, "Introduction to the Rarer Elements.")
† International atomic weights, 1916.

DETECTION

The samples having been brought into solution by one of the methods detailed under preparation and solution of the sample, the elements may be detected by one of the following tests:

Spectroscopic. Many of the rare earth's elements have either characteristic spark spectrums or absorption spectrums and their presence may be detected by this means.

Yttrium,	no	absorption	spectrum;	gives	brilliant	spark	spectrum.
Erbium,	gives	"	"	"	"	"	"
Ytterbium,	no	"	"	"	"	"	"
Terbium,	no	"	"	"	"	"	"
Cerium,	no	"	"	"	"	"	"
Lanthanum,	no	"	"	"	"	"	"
Samarium,	gives	"	"	no	spark	spectrum.	
Scandium,	no	"	"	"	"	"	
Praseodymium,	no	"	"	"	"	"	
Neodymium,	no	"	"	"	"	"	

Cerium shows lines of greatest intensity in the arc spectrum at 4337.9, 4527.5, 4386.9, 4594.1. In the spark spectrum at 4460.3, 4562.5, 4572.4, 4594.1, 4628.3. All of these lines are in the visible spectrum.

[1] Research Chemist, New York City.

In the wet way cerium may be detected when in the form of cerium nitrate by boiling with lead peroxide and nitric acid. A deep yellow color is imparted to the solution, due to the formation of ceric nitrate.

Cerium may be detected by the addition of sodium hypochlorite to the solution of a colorless cerous salt. Red ceric hydroxide is precipitated. The test may be confirmed by the chlorine gas evolved when the precipitate is dissolved in hydrochloric acid.

Cerous salts are precipitated by fixed alkalies and are insoluble in excess. Tartaric acid hinders the precipitation. Ammonium sulphide also precipitates the hydroxide. Oxalic acid precipitates cerous oxalate, white, from moderately acid solutions. It is soluble in hot ammonium oxalate but precipitated by dilution with cold water.

Lanthanum may be detected by adding iodine to the washed precipitate, formed by the addition of ammonium hydroxide to a solution of its salts. A characteristic blue coloration results.

Praseodymium, neodymium, may be detected by the reddish color of their solutions also by the rose red or violet color imparted to a bead of microcosmic salt when heated in the flame of a blow pipe.

Scandium. The hydrochloric acid solution of a scandium salt, when boiled for thirty minutes with solid Na_2SiFl_6 gives a precipitate which is free from all the other rare earths, the scandium taking the place of the sodium in the compound.

Ytterbium may be detected by adding to a neutral solution $H_2SeO_3 \cdot 4H_2O$. A white precipitate of $Yb_2(SeO_3)_3$, which is insoluble, results.

Erbium. In the flame test this earth gives an intense green light.

ESTIMATION

The estimation of the rare earths is not required, other than Cerium, at the present time except in a few special instances as the various elements have found but limited commercial applications. They have all been separated from their native combinations, but only a few have been isolated and many are still believed to be combinations of elements.

Cerium enters into the manufacture of Welsbach mantles; in the form of $Ce_2(SO_4)_3$ it is used in the manufacture of aniline black; as oxalate, it is used in medicine, and as metal in alloys.

Yttrium is employed in the fabrication of Nernst lamp filaments and gas mantles.

The most important ores which contain the rare earth elements are:

Monazite, $(Ce, La, Di, Th)_2PO_4$,	raw material for	Ce, La.	
Gadolinite, $Be_2FeY_2Si_2O_{10}$,	" "	Yt earths.	
Xenotime, $YtPO_4$,	" "	Yt	"
Euxenite, $R'''(NbO_3)_3 \cdot R_2'''(TiO_3)_3 \cdot 3/2H_2O$,	" "	Yt	"
Cerite, $(Ca, Fe)(CeO)(Ce_2 \cdot 3OH)(SiO_3)_3$,	" "	Ce	"
Samarskite, $R_3''R_2'''(Nb, Ta)_6O_{21}$,	" "	Yt	"
Yttrotantalite, $R''R_2'''(Nb, Ta)_4O_{15} \cdot 4H_2O$,	" "	Yt	"
Sipylite, complex,	" "	Yt	"
Keilhauite, complex silicate,	" "	Yt	"

In the formulas given above R'' stands for any dibasic radical or element while R''' stands for any tribasic radical or element.

Preparation and Solution of the Sample

1. Fusion Method. The finely pulverized sample is fused with sodium carbonate and the melt after cooling is extracted with cold water. A sufficient quantity of hydrochloric acid to impart an acid reaction is added. The solution obtained is evaporated to dryness and baked to dehydrate the silica, then treated with a little hydrochloric acid and after dilution with water, filtered. Ammonia water is added to the solution in slight excess and the solution allowed to stand until the precipitate has settled. It is then filtered off, washed with cold water and dissolved in hydrochloric acid. All of the rare earths are then present in the solution as chlorides.

2. Acid Extraction. Decomposition of the finely pulverized sample may be effected by mixing it with a sufficient quantity of sulphuric acid to make a paste and then heating the mass, slowly at first and then gradually increasing the heat to dull redness when fumes of SO_3 appear. After cooling, the mass is extracted with cold water and the metals of the H_2S group removed in the usual way. The rare earths are then present in the solution as sulphates and may be separated by one of the methods detailed below.

3. Acid Extraction. A strong mixture of nitric acid and hydrochloric acid may be used to effect the decomposition of some of the minerals. The solution after being evaporated to dryness and baked leaves a residue which contains the mixed rare earths. The rare earths are dissolved in dilute hydrochloric acid. Any silica present is filtered off and the rare earths present in the clear solution may be separated by one of the methods detailed below.

4. Decomposition by Means of Hydrofluoric Acid.[1] Samarskite and euxenite in the finely powdered state are moistened with their own weight of water and twice as much fuming hydrofluoric acid. The attack takes place in a few seconds. When the violent action is over the solution is evaporated to dryness on the steam bath, taken up with water (30 to 40 cc. for a 5-gram sample) and the contents of the dish filtered and washed. The mineral is then divided into two portions, the filtrate containing all the metallic acids, iron and manganese, the insoluble portion containing all the rare earths and uranic acid.

The difficulty of attack increases in proportion to the amount of tantalic acid present in the sample. The rare earths are then extracted from the incoluble portion by one of the methods previously mentioned. Fusion with sodium carbonate is preferred.

SEPARATIONS

Separation of the rare earths from iron, aluminum and thorium[2] may be effected by adding sodium fluoride to the hydrochloric acid solution of the Iron Group which has been precipitated as hydroxide. The precipitate, which consists of the double fluorides of the rare earths and thorium, is washed thoroughly and evaporated with sulphuric acid on the sand bath to decompose the fluorides. This process removes the alkaline earths as insoluble sulphates. The excess acid is removed by fuming and the solution of the sulphates after diluting and warming is treated with sodium thiosulphate in solution. Thorium thiosulphate is precipitated. In solution are the sulphates of all the rare earths. Scandium

[1] Prescott and Johnson.
[2] Browning's "Introduction to the Rarer Elements."

is also precipitated as thiosulphate if the solution in sulphuric is fumed too long and a neutral solution results.

Calcium and manganese, which may also come down with an oxalate precipitate of the rare earths, may be separated from the earths of the yttrium group by precipitation of the solution with oxalic acid, filtering off the precipitate, dissolving it in nitric acid and evaporating to dryness to decompose the manganese salts. Extracting with water leaves the manganese in the residue. Treat the filtrate with ammonia water. The yttrium group precipitates as hydroxides and may be filtered from the calcium, which remains in solution.

Cerium, lanthanum, praseodymium, neodymium, europium and gadolinium may be separated from the other rare earths by adding a saturated solution of potassium sulphate to the sulphate or chloride solution of all of the rare earths. The above-mentioned elements form insoluble double salts.

Scandium may be separated from **yttrium** by boiling a solution of the nitrates. A basic scandium nitrate is first precipitated.

Yttrium Group. Barium carbonate forms no precipitate in the cold, hence the elements comprising same may be separated from aluminum, iron, chromium, thorium, cerium, lanthanum, praseodymium, and neodymium by this means.

Yttrium Group. The precipitation of the group as hydroxides is not affected by the presence of tartaric acid. Hence the members may be thus separated from aluminum, glucinum, thorium, zirconium, and iron.

Praseodymium, neodymium, lanthanum, and samarium may be separated from each other by the fractional precipitation of a dilute solution of the nitrates with a very dilute solution of ammonia water (1 gram of NH_3 in 500 cc.). The first precipitates are rich in samarium; the didymiums come down next and the lanthanum in the last portions. By a continual repetition nearly pure salts may be obtained.

Besides the separations mentioned above the group members may be freed from each other by various other methods, as for example:

(1) Fractional crystallization of the picrates.
(2) Fractional crystallization of the double magnesium nitrates.
(3) Fractional precipitation of the oxalates in a nitric acid solution, etc.

GRAVIMETRIC ESTIMATIONS

Owing to the fact that the quantitative separation of the rare earths is only accomplished by the expenditure of a vast amount of time and labor and that the various elements with the exception of but few have found no commercial application, exact methods have not been worked out for the various quantitative assays.

Cerium, however, which is the most important, may be determined as follows:

The element having been brought into solution by one of the methods detailed above and separated from the base metals, silica and thorium may be isolated from the other rare earths by precipitation in a slightly acid solution with oxalic acid. The precipitate is allowed to settle twenty-four hours, filtered, washed with water and ignited. The oxides are then dissolved in hydrochloric acid and precipitated as hydroxide by the addition of an excess of caustic potash. The

precipitate, suspended in solution, is subjected to the action of chlorine gas which is bubbled through in a steady stream. All of the rare earths except cerium are converted into the chlorides, while the latter remains as a reddish, gelatinous precipitate, ceric hydroxide—($Ce(OH)_4$). This may be filtered off, washed, ignited and weighed as oxide (CeO_2).

Cerium may be determined in its salts by precipitation with oxalic acid, allowing to settle out, filtering, washing, and igniting to the oxide.

VOLUMETRIC METHOD FOR THE DETERMINATION OF CERIUM

Method of Franz Stolba.[1] The cerium having been separated from all of the other rare earths by some procedure, as, for example, that outlined above under Gravimetric Determination, may be precipitated as ceric oxalate. (Dissolving the hydroxide in hydrochloric acid and then precipitating with oxalic acid.) The oxalate precipitate is filtered off, washed with water until free from hydrochloric acid, and transferred to a beaker containing a small quantity of sulphuric acid and a sufficient quantity of water. The mixture is warmed to about 70° C. and titrated with a standard solution of $KMnO_4$. During the process of titration the quantity of undissolved matter diminishes and the change of color at the end is very distinct. The solution of $KMnO_4$ used is previously standardized, using a known amount of pure ceric sulphate and the same quantities of water and sulphuric acid.

Determination of Cerium in Welsbach Mantles. Colorimetric Method[2]

Burn off the organic matter and heat with about three times their own weight of H_2SO_4 (conc.) on a sand bath. Allow to cool and pour into 20 cc. of water. In twenty-four hours the sulphates are completely dissolved and the solution after neutralizing the excess of acid with ammonia water is precipitated with oxalic acid. The oxalates after settling out are filtered, washed, transferred to a porcelain casserole and digested with nitric acid, a little being added at a time until complete decomposition has taken place. Evaporate to dryness to remove the excess acid. The nitrates of cerium and thorium are dissolved in water and made to volume. Aliquots are then taken and diluted in comparison tubes, 1 cc. H_2O_2 (Merck's perhydrol) is added. On adding ammonia water Th(OH) is colored orange in proportion to the amount of cerium present. In dilute solutions citric acid prevents the precipitation of the hydroxides and the color can be easily compared with standards containing known amounts.

[1] Crooke's "Select Methods of Analysis."
[2] Method of E. Benz, Z. angew Chem., 16, 300, 1902.

RARE EARTH OXALATES

Convert into the sulphates by evaporating with sulphuric acid. Dissolve in water and add solid sodium sulphate in excess to the nearly neutral solution.

(1) PRECIPITATE:

Th, Ce, La, Pr, Nd, Sa, Eu, Gd, etc., as double sodium sulphates.
Boil with an excess of sodium hydroxide, filter, wash with hot water and dissolve in nitric acid. Treat the nitrates with an excess of zinc oxide and potassium permanganate.

(1) FILTRATE:

As double sodium sulphates. Yt, Tb, Dy, Ho, Er, Tm, Yb, Sc, etc.
Add oxalic acid in excess to precipitate the earths as oxalates.

(3) PRECIPITATE:

CeO_2 and $ThO_2 \cdot MnO_2$ is present is removed by solution in hydrochloric acid and then precipitation of the Ce and Th as double sulphates with sodium.
Precipitate is boiled with an excess of sodium hydroxide, washed with hot water and dissolved in nitric acid. Add ammonia and ammonium oxalate and ammonium acetate.

PRECIPITATE:	FILTRATE:
Cerium oxalate. Treat with excess of zinc oxide and solution of potassium permanganate. Cerium oxide precipitates. Dissolve in hydrochloric acid and precipitate cerium as oxalate with oxalic acid.	Thorium oxalate is treated with ammonia in excess, ignite. ThO_2.

(3) FILTRATE:

Saturate the solution with sodium sulphate and wash the precipitate formed with a solution of sodium sulphate.

PRECIPITATE:	FILTRATE:
Boil with excess of sodium hydroxide, filter and wash with hot water. Dissolve in a known amount of nitric acid and add an equivalent amount of magnesium nitrate in solution. Evaporate the solution until upon blowing on surface small crystals form. Spray water on surface and allow to crystallize. *Lanthanum* crystallizes 1st, *Praseodymium* crystallizes 2d, *Neodymium* crystallizes 3d *Samarium* crystallizes 4th *Europium* crystallizes 5th *Gadolinium* crystallizes 6th The crystallization is controlled by the spectroscope. The greater number of times the earths are fractionated the purer the product will be.	Combine with filtrate No. 1.

(2) PRECIPITATE:

As an excess of sulphuric acid and evaporate to form anhydrous sulphates of Yt, Tb, drous sulphates of Yt, Yb, Dy, Ho, Er, Tm, Sc, Yb, etc.
Dissolve in cold water and pour over an excess of barium bromate. Stir well and place on the hot water bath. When double decomposition is complete (when the liquid gives no further precipitate with barium bromate solution after diluting and boiling), the mass is filtered and evaporated to crystallization.
Terbium crystallizes 1st, *Dysprosium* crystallizes 2d, *Holmium* crystallizes 3d, *Yttrium* crystallizes 4th, *Erbium* crystallizes *Thulium* 5th, crystallizes 6th
The mother liquor is made neutral with ammonia and saturated with potassium sulphate.

PRECIPITATE	FILTRATE:
Scandium. Potassium Sulphate.	Add oxalic acid. *Ytterbium* is precipitated as oxalate.

(2) FILTRATE:

Add to filtrate No. 3.

CHLORINE

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Cl_2, *at.wt.* 35.46; *D.* (*air*), 2.491; *m.p.* −101.5°;[1] *b.p.* −33.6° C.; *oxides* Cl_2O, ClO_2, Cl_2O_7.

DETECTION

Free Chlorine. The yellow gas is recognized by its characteristic odor. It liberates iodine from iodides; it bleaches litmus, indigo, and many organic coloring substances.

Chlorides. Silver Nitrate Test. In absence of bromides and iodides, which also form insoluble silver salts, silver nitrate precipitates from solutions containing chlorides white, curdy, silver chloride, AgCl (opalescent with traces), soluble in NH_4OH (AgBr slowly soluble, AgI difficultly soluble), also soluble in concentrated ammonium carbonate (AgBr is very slightly soluble; AgI is insoluble). Silver chloride turns dark upon exposure to light.

Free Hydrochloric Acid. Manganese Dioxide, Potassium Permanganate, and certain oxidizing agents liberate free chlorine gas when added to solutions containing free hydrochloric acid. The gas passed into potassium iodide liberates free iodine, which produces a blue solution with starch.

Concentrated Sulphuric Acid added to chlorides and heated liberates HCl gas, which produces a white fume in presence of ammonium hydroxide.

Detection in Presence of Cyanate, Cyanide, Thiocyanate. An excess of silver nitrate is added to the solution, the precipitate filtered off and boiled with concentrated nitric acid to oxidize the cyanogen compounds and the white precipitate, silver chloride, subjected to the tests under chlorides to confirm the compound.

Detection in Presence of Bromide and Iodide. About 10 cc. of the solution is neutralized in a casserole with acetic acid, adding about 1 to 2 cc. in excess, and then diluting to about 6 volumes with water. About half a gram of potassium persulphate, $K_2S_2O_8$, is added and the solution heated. Iodine is liberated and may be detected by shaking the solution with carbon disulphide, which is colored blue by this element. Iodine is expelled by boiling, the potassium persulphate being repeatedly added until the solution is colorless. Bromine is liberated by adding 2 or 3 cc. of dilute sulphuric acid and additional persulphate. A yellowish-red color is produced by this element. Carbon disulphide absorbs bromine, becoming colored yellowish red. Bromine is expelled with additional persulphate and by boiling. The volume of the solution should be kept to about 60 cc., distilled water being added to replace that which is expelled by boiling. When bromine is driven out of the solution, the silver nitrate test for chlorides is made. A white, curdy precipitate, soluble in ammonium hydroxide and reprecipitated upon acidifying with nitric acid, is produced, if chlorides are present.

[1] Ref. Cis. 35 (2d Ed.), U. S. Bureau of Standards.

If Chlorates are Present. The halogens are precipitated with silver nitrate, the precipitate dissolved with zinc and sulphuric acid and the solution treated as directed in the preceding paragraph.

Test for Hypochlorite. Potassium hypochlorite, KClO, shaken with mercury forms the yellowish-red compound Hg_2OCl_2,[1] which does not form with the other potassium salts of chlorine, i.e., KCl, $KClO_2$, $KClO_3$, $KClO_4$.

Hypochlorites decolorize indigo, but do not decolorize potassium permanganate solutions. If arsenious acid is present, indigo is not decolorized until all of the arsenious acid has been oxidized to the arsenic form.

Tests for Chlorite. Potassium permanganate solution is decolorized by chlorites. (The solution should be dilute.)

A solution of indigo is decolorized, even in presence of arsenious acid (distinction from hypochlorites).

Detection of Chlorate. The dry salt heated with concentrated sulphuric acid detonates and evolves yellow fumes.

Chlorates liberate chlorine from hydrochloric acid.

Perchlorate. The solution is boiled with hydrochloric acid to decompose hypochlorites, chlorites and chlorates. Chlorides are removed by precipitation with silver nitrate, the filtrate evaporated to dryness, the residue fused with sodium carbonate to decompose the perchlorate to form the chloride, which may now be tested as usual.

ESTIMATION

The determination of chlorine is required in a large number of substances. It occurs combined as a chloride mainly with sodium, potassium and magnesium. Rock salt, NaCl, sylvine, KCl, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, matlockite, $PbCl_2 \cdot PbO$; horn silver, AgCl, atacamite, $CuCl_2 \cdot 3Cu(OH)_2$, are forms in which it is found in nature. Chlorine is determined in the evaluation of bleaching powder. It is estimated in the analysis of water.

Preparation and Solution of the Sample

In dissolving the sample the following facts should be borne in mind: Although chlorides are nearly all soluble in water, silver chloride is practically insoluble (100 cc. dissolves 0.000152 gram at 20° C.); mercurous chloride is nearly as insoluble as silver chloride (0.00031 gram); lead chloride requires heat to bring it into solution (in cold water only 0.673 gram soluble per 100 cc. of water). Chlorides of antimony, tin, and bismuth require free acid to keep them in solution. Hydrochloric acid increases the solubility of silver, mercury, lead, antimony, bismuth, copper (Cu′), gold and platinum, but decreases the solubility of cadmium, copper (Cu″), nickel, cobalt, manganese, barium, calcium, strontium, magnesium, thorium, sodium, potassium and ammonium chlorides.

Chlorine gas is most readily dissolved in water at 10° C. (1 vol. H_2O dissolves 3.095 vols. Cl). Boiling completely removes chlorine from water.

Hypochlorites, chlorites, chlorates, and perchlorates are soluble in water.

The chlorine may be present either combined or free. In the combined state it may be present as free hydrochloric acid or as a water-soluble or insoluble salt.

[1] Prescott and Johnson, Qual. Chem. Anal. D. Van Nostrand Co.

Water-soluble Chlorides. Chlorides of the alkali or alkaline earth groups may be treated directly with silver nitrate upon making slightly acid with nitric acid, the chlorine being determined either gravimetrically or volumetrically according to one of the procedures given later. It is convenient to work with samples containing 0.01 gram to 1 gram of Cl. The sample is dissolved in about 150 cc. of water, made acid with nitric acid with about 5 to 10 cc. in excess of the point of neutralization, should the sample be alkaline. Then the chlorine combined as chloride is determined as directed later.

If the water solution contains a chloride of a heavy metal which forms basic salts (e.g., stannic, ferric, etc., solutions), or which may tend to reduce the silver solution, it is necessary to remove these by precipitation with ammonium hydroxide, or by sodium hydroxide, or potassium carbonate solution. The salt is dissolved in water and acidified with HNO_3, adding about 10 cc. in excess, for about 150 cc. of solution. (This excess HNO_3 should be sufficient to oxidize substances which would tend to reduce the silver reagent; e.g., $FeSO_4$, etc.) Ammonia solution (free from chloride) is added in sufficient quantity to precipitate the heavy metals iron, manganese, aluminum, etc. The mixture is filtered and the residue washed several times with distilled water. Chlorine is determined in the filtrate by acidifying with HNO_3 as directed above.

Water-insoluble Chlorides. The chloride may frequently be decomposed by boiling with sodium carbonate solution. Many of the minerals, however, require fusion with sodium carbonate to prepare them for solution; e.g., apatite, sodalite, etc. Silver chloride may also be decomposed by fusion.

Silver Chloride. The sample is mixed with about three times its weight of Na_2CO_3 and fused in a porcelain crucible until the mass has sintered together. The soluble chloride, NaCl, is leached out with water, leaving the water-insoluble carbonate of silver, which may be filtered off. The filtrate is acidified with HNO_3 and chlorine determined as usual.

Chlorine in Rocks. The finely ground material is fused with about five times its weight of potassium carbonate. The melt is extracted with hot water, cooled and the solution acidified with nitric acid (methyl orange indicator), and the solution allowed to stand several hours (preferably over night). If silicic acid precipitates, the solution is treated with ammonia and boiled, filtered and the filter washed with hot water. The cooled filtrate is acidified with nitric acid and chlorine determined as usual. If silicic acid does not separate, the addition of ammonia may be omitted and chlorine determined in the solution.

Free Chlorine. Free chlorine may be determined volumetrically according to the procedure given under this section. If it is desired to determine this gravimetrically, a definite amount of the chlorine water is transferred by means of a pipette to a flask containing ammonia solution and the mixture heated to boiling. The cooled solution is acidified with nitric acid and the chloride precipitated with silver nitrate according to the standard procedure given on page 127.

NOTE. Free chlorine cannot be precipitated directly, as the following reaction takes place: $6Cl+6AgNO_3+3H_2O=5AgCl+AgClO_3+6HNO_3$.

Reaction of chlorine with ammonia: $2Cl+2NH_4OH=NH_4Cl+NH_4OCl+H_2O$. When the solution is boiled, NH_4OCl breaks down, e.g, $3NH_4OCl+2NH_3=3NH_4Cl+N_2+3H_2O$.

Chlorine in Ores and Cinders. One hundred grams of the finely ground ore or cinder are placed in a 500-cc. flask, containing 300 cc. of strong sulphuric

id (Cl-free). The flask is shaken to mix the sample with the acid and then nnected with an absorption apparatus, containing distilled water or dilute ustic solution. The sample is gradually heated, the distillation flask resting pon a sand bath. After two hours, which is sufficient to expel all the chlorine hydrochloric acid, the contents of the absorption tubes are filtered, if free lphur is present (sulphide ores), nitric acid added and the filtrate brought boiling to oxidize any SO_2 that may be present. Chlorine is precipitated cording to the standard procedure on page 124.

During the run the distilling flask should be shaken occasionally to prevent king. Suction applied at the absorption end of the apparatus and a current air swept through the system aids in carrying over the HCl into the water NaOH.

etermination of Halogens in Organic Compounds. Method of Carius[1]

Organic compounds are decomposed by heating with concentrated nitric acid high temperatures under pressure. If this heating is conducted in the resence of silver nitrate, the halogen hydride, formed by the action of nitric id on the organic compound, is converted to the silver halide as fast as the alogen hydride is formed. Arsenic, phosphorus, and sulphur are oxidized to rsenic, phosphoric, and sulphuric acids, the metals present being converted nitrates.

Procedure. About 0.5 to 1 gram of powdered silver nitrate is introduced, y means of a glazed paper funnel, into a heavy-walled, bomb-glass tube, which sealed at one end and is 50 cm. long, 2 cm. in diameter and about 2 mm. thickess of wall. About 40 cc. of strong nitric acid (sp.gr. 1.5), free from chlorine, re introduced by means of a long-stemmed funnel, to avoid wetting the upper ortion of the tubing. About 0.15 to 0.2 gram of the substance, contained a small glass tube closed at one end (5 cm. long, 5 mm. in diameter), is introuced into the bomb tube, inclined to one side. The small tube should float in e nitric acid, as it is important that the material should not come in ntact with nitric acid until the bomb has been sealed, as loss of halogen apt to occur with open tubes. The upper end of the bomb is softened in e blast-lamp flame, drawn out to a thick-walled capillary tube and the passage sed.

When cold the bomb is wrapped in asbestos paper, shoved into an iron antle of a bomb furnace and the heat turned on. The heating is so regulated at the temperature is raised to 200° C. in three hours. If a higher temperare is necessary, the heating should be such as to cause a rise of 50° C. in three ours. Substances of the aromatic series require eight to ten hours heating at 50 to 300° C., while aliphatic substances may be decomposed at 200° C. in bout four hours. Occasionally it is necessary to relieve the pressure in a ibe after heating to 200° C., before taking to a higher temperature, by softening e tip of the cooled bomb in a flame, allowing the accumulated gas to blow ut, resealing and again heating to the desired temperature. Decomposition complete when neither crystals nor drops of oil are evident in the tube. hen the bomb is cooled, it is removed by taking out the iron sheath from the

[1] Ann. d. Chem. u. Pharm. (1865), **136**, p. 129.

furnace and inclining it so that the glass capillary tip slides partly out of the tube. (The eyes should be protected by goggles.) The point of the capillary is held in the flame until the tip softens and the gas pressure is released by blowing through a passage in the softened glass. When the gas has escaped, a scratch with a file is made below the capillary and the tip broken off by touching the scratch with a hot glass rod. The contents of the bomb are poured out into a beaker, the tube washed out with water and the combined solution made to about 300 cc. This is heated to boiling and then allowed to cool. The halide precipitate is filtered through a Gooch crucible, then dried and weighed.

If pieces of glass should be present, the precipitates, AgCl or AgBr, are dissolved in ammonium hydroxide, filtered and reprecipitated by acidifying with nitric acid. AgI may be dissolved by means of dilute sulphuric acid and zinc. The excess zinc is removed, the glass washed free of iodine, dried and weighed and its weight subtracted from the original impure AgI, giving the weight of the pure silver iodide.

Lime Method for Determination of Halogens in Organic Matter

A layer of lime (free from chloride), about 6 cm. long, is introduced into a difficultly fusible glass tube, closed at one end (40 cm. long and with 1 cm. bore), followed by 0.5 gram of the substance, and 5 cm. more of the lime. The substance is thoroughly mixed by means of a copper wire with a spiral end. The tube is now nearly filled with lime, then placed on its side and gently tapped to cause the lime to settle and form a small canal above the layer. The tube is placed in a small carbon combustion furnace. The heat is turned on, so that the front end of the tube is heated to dull redness and then the end containing the substance. When the organic matter has been decomposed, the tube is cooled and the contents transferred to a beaker and the lime dissolved in dilute nitric acid (Cl-free). The carbon is filtered off and the halogen determined as usual in the filtrate.

If calcium sulphate is present in the lime, it is reduced to the sulphide by the organic matter, so that AgS will be precipitated along with the halides. To prevent this, hydrogen peroxide is added to the solution which should be slightly alkaline. The mixture is boiled to remove the excess of H_2O_2 and is then acidified with nitric acid, the solution filtered and the halide determined in the filtrate.

With substances rich in nitrogen, some soluble cyanide will be formed. The silver precipitate containing the halides and the cyanide is heated to fusion. The residue is now treated with zinc and sulphuric acid, the metallic silver and the paracyanogen filtered off and the halides determined in the filtrate.

Sodium Peroxide Method

Organic compounds may be decomposed by sodium peroxide in an open crucible without recourse to a sealed tube, as is required by the Carius method. The following is the procedure outlined by Pringsheim.[1]

About 0.2 gram of substance in a small steel crucible is treated with a cal-

[1] C. N., 1905, 91, 2372, 215.

culated quantity of sodium peroxide.[1] The crucible should be only two-thirds of its height full; this is put in a large porcelain crucible, in which a little cold water is carefully placed, so that the steel crucible stands out 1 to 2 cm. This latter crucible is covered with its own cover, in which is a hole through which an iron wire heated to redness can be introduced with the object of starting the combustion. As soon as the combustion is completed the whole is plunged into the water in the larger crucible. The porcelain crucible is covered with a watch-glass and heated gently until the whole mass is dissolved. This point is recognized when no more bubbles are given off and when there are no more particles of carbon which have escaped combustion. The steel crucible is then removed and washed carefully; the solution is filtered and treated with an excess of sulphurous acid (to neutralize the alkaline liquid, and to reduce the oxidized products: bromic, iodic acids, etc.). The solution is acidulated with nitric acid, then made to a volume of about 500 cc., and the halogens precipitated with silver nitrate and the precipitate washed, dried and weighed as usual.

SEPARATIONS

Separation of Chlorine and the Halides from the Heavy Metals. Halides of the heavy metals are transposed by boiling their solutions with sodium carbonate, the heavy metals being precipitated as carbonates and the halides going into solution as sodium salts.

Separation of Halides from Silver and from Silver Cyanide. The silver salt is treated with an excess of zinc and sulphuric acid, the metallic silver and the paracyanogen filtered off, and the halides determined in the filtrate.

Separation of the Halides from One Another. Separation of Chlorine from Iodine. The method depends upon the fact that nitrous acid sets iodine free from dilute solutions containing a mixture of halogen salts, bromides and chlorides being unaffected. $2KI+2KNO_2+4H_2SO_4=4KHSO_4+2NO+2H_2O+I_2$.

The solution of the chloride and the iodide in an Erlenmeyer flask is diluted to 400 cc. and 10 cc. of dilute sulphuric acid, 1 : 1, are added. The gas from 2 grams of sodium nitrite is passed into the solution at the rate of about five bubbles per second.[2] (Pure sodium or potassium nitrite may be added directly to the solution in the flask.) The liberated iodine is now completely expelled by boiling until the evolving steam no longer reacts upon litmus paper. Should a determination of iodine be desired the evolved gas is absorbed in a hydrogen peroxide sodium hydroxide solution according to the procedure described under iodine.[3]

[1] Charge of sodium peroxide is judged as follows:

Per cent C and O in material.	Amount of sugar to add.	Amount of Na_2O_2 required.
Over 75	0	18 times wt. of sub.
30 to 75	0	16 times wt. of sub.
25 to 50	½ the wt. of sub.	16 times wt. of sub.
Below 25	An equal weight	16 times wt. of sub.

[2] Nitrous acid is generated by addition of dilute H_2SO_4 to $NaNO_2$, the acid being added drop by drop through a thistle tube with glass stop-cock.

[3] Method of Jannasch, see chapter on Iodine.

The contents of the flask are treated with silver nitrate and the precipitate silver chloride determined as usual.

Separation of Chlorine and Bromine from Iodine. The procedure is similar to the separation of chlorine from iodine with the exception that a more dilute solution is necessary to prevent the volatilization of bromine with the iodine.

The neutral solution containing the halogens is diluted to about 700 cc. and about 2 to 3 cc. of dilute sulphuric acid, 1 : 1, are added and a sufficient amount of pure sodium nitrite introduced or nitrous acid gas passed into the solution as directed above. The solution is boiled until colorless and until the evolved steam no longer acts upon litmus paper. About twenty minutes' boiling after the color of iodine has disappeared from the flask will completely eliminate the iodine; in this case, however, water should be added to the flask to replace that evaporated before the solution has been reduced to a volume of less than 600 cc.

For determination of bromine in the residue remaining in the flask, see the chapter on this subject, page 79.

GRAVIMETRIC METHOD

Determination of Chlorine Combined as Chloride by Precipitation as Silver Chloride

The procedure is the reciprocal to the one for determination of silver; in this case the soluble silver salt is added to the sodium chloride solution, in which chlorine is to be determined.

Procedure. To the nitric acid solution of the chloride, prepared according to directions given under "Preparation and Solution of the Sample," is added silver nitrate solution in slight excess, stirring during the addition of the reagent. (Stirring aids the coagulation of the AgCl and hastens settling. It is advisable to allow the precipitate to settle sufficiently to clear the upper portion of the solution in order to detect whether further precipitation takes place upon addition of more of the reagent.) The mixture is now heated until it is hot to the touch and then allowed to settle for half an hour or more, preferably in the dark. It is filtered through a weighed Gooch crucible, washing the precipitate by decantation several times with cold water, slightly acid with nitric acid, and then the precipitate transferred to the Gooch is washed free of silver nitrate (HCl test) with cold distilled water. The Gooch is dried for fifteen to twenty minutes at 100° C. and then at about 130° C. to constant weight. The sample is now weighed as AgCl.[1]

$$AgCl \times 0.2474 = Cl.$$

NOTES. Free chlorine is converted to chloride according to the procedure given for preparing the sample, and then determined according to the procedure given above. If chlorine and chlorides are both present in the solution and each is desired, the free chlorine is determined according to the volumetric procedure given later, and the total chloride determined gravimetrically, then free chlorine subtracted from total chlorine and the result taken as combined chlorine of the solution.

[1] The silver chloride should be completely soluble in ammonia. If it is not, the product is impure. To separate it from SiO_2, Al_2O_3, and other impurities, the precipitate is dissolved in ammonia, the solution filtered free from the impurities, and the AgCl reprecipitated by acidifying with nitric acid and adding a few drops of silver nitrate.

If a paper filter is used in place of the Gooch crucible, the greater part of the precipitate is removed, the paper ignited separately, the reduced silver oxidized with HNO_3, a drop or so HCl added, then evaporated off, and the residue combined with major portion of AgCl and ignited gently until the salt begins to melt.

VOLUMETRIC METHODS

Determination of Chlorine in Acid Solution, Silver Thiocyanate Ferric Alum Method

The method, devised by Volhard,[1] is applicable to titration of chlorine in acid solutions, a condition frequently occurring in analysis, where the Silver-Chromate Method of Mohr cannot be used. The method is based on the fact that when solutions of silver and an alkali thiocyanate are mixed in presence of a ferric salt, the thiocyanate has a selective action towards silver, combining with this to form thiocyanate of silver, any excess of that required by the silver reacting with the ferric salt to form the reddish-brown ferric thiocyanate, which color serves as an indication of the completion of the reaction. An excess of silver nitrate is added to the nitric acid solution containing the chloride, AgCl filtered off, and the excess of silver titrated with the thiocyanate in presence of the ferric salt.

Copper (up to 70%), arsenic, antimony, cadmium, bismuth, lead, iron, zinc, manganese, cobalt, and nickel, do not interfere, unless the proportion of the latter metals is such as to interfere by intensity of the color of their ions.

Preparation of Special Reagents. ***N/10 Ammonium or Potassium Thiocyanate Solution.*** About 8 grams of ammonium or 10 grams of potassium salt are dissolved in water and diluted to one liter. The solution is adjusted by titration against the N/10 silver nitrate solution. It is advisable to have 1 cc. of the thiocyanate equivalent to 1 cc. of the silver nitrate solution. Owing to the deliquescence of the thiocyanates the exact amount for an N/10 solution cannot be weighed.

N/10 Silver Nitrate. This solution contains 10.788 grams Ag or 16.989 grams $AgNO_3$ per liter. The silver nitrate salt, dried at 120° C., or pure metallic silver may be taken, the required weight of the latter being dissolved in nitric acid and made to volume, or 17.1 grams of the salt dissolved in distilled water and made to 1000 cc. The solution is adjusted to exact decinormal strength by standardizing against an N/10 sodium chloride solution, containing 5.846 grams of pure NaCl per liter.

Ferric Indicator. Saturated solution of ferric ammonium alum. Should this not be available, $FeSO_4$ may be oxidized with nitric acid, and the solution evaporated with an excess of H_2SO_4 to expel the nitrous fumes. A 10% solution is desired. Five cc. of either of these reagents are taken for each titration.

Pure Nitric Acid. This should be free from the lower oxides of nitrogen. Pure nitric acid is diluted to contain about 50% HNO_3, and boiled until perfectly colorless. The reagent should be kept in the dark. Dilute nitric acid does not interfere with the method.

Procedure. To the solution, containing 0.003 to 0.35 gram chlorine, in combination as a chloride, is added sufficient of the pure HNO_3 to make the solution acid and about 5 cc. in excess. To the solution, diluted to about 150 cc., is added an excess of standard silver nitrate reagent. The precipitated AgCl

[1] Liebig's Ann. d. Chem., **190**, 1; Sutton, "Volumetric Analysis," 10 Ed.

is filtered off and washed free of silver nitrate. The filtrate and washings are combined and titrated with standard thiocyanate.[1]

The filtrate from the precipitated chloride is treated with 5 cc. of the ferric solution,[2] and the excess silver determined by addition of the thiocyanate until a permanent reddish-brown color is produced. Each addition of the reagent will produce a temporary reddish-brown color, which immediately fades as long as silver uncombined as thiocyanate remains. The trace of excess produces ferric cyanate, the reddish-brown color of this compound being best seen against a white background. From this titration the amount of silver nitrate used by the chloride is ascertained.

One cc. N/10 $AgNO_3$ = 0.00355 gram Cl or 0.00585 gram NaCl.

Volumetric Determination of Chlorine in a Neutral Solution, Silver Chromate Method

The method, worked out by Fr. Mohr,[3] is applicable for determination of chlorine in water or in neutral solutions containing small amounts of chlorine, the element should be present combined as a soluble chloride. Advantage is taken of the fact that silver combines with chlorine in presence of a chromate, Ag_2CrO_4 being decomposed as follows: $Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$. When all the chlorine has gone into combination as AgCl, an excess of K_2CrO_4 immediately forms the red Ag_2CrO_4, which shows the reaction of $AgNO_3$ with the chloride to be complete.

Reagents. ***Tenth Normal Silver Nitrate Solution.*** Theoretically 16.988 grams $AgNO_3$ per liter are required. In practice 17.1 grams of the salt are dissolved per 1000 cc. and the solution adjusted against an N/10 NaCl solution containing 5.846 grams NaCl per liter.

Potassium Chromate. Saturated solution.

Procedure. To the neutral solution (made so, if necessary, by addition of nitric acid or ammonium hydroxide), are added 2 or 3 drops of the potassium chromate solution. A glass cell[4] (or a 50-cc. beaker) is filled to about 1 cm. in depth with water tinted to the same color as the solution being titrated. The cell is placed on a clear glass plate half covering the casserole containing the sample. The standard silver solution is now added to the chloride solution from a burette until a faint blood-red tinge is produced, the red change being easily detected by looking through the blank, colored cell.

One cc. N/10 K_2CrO_4 = 0.003546 gram Cl.

NOTES. Chlorides having an acid reaction ($AlCl_3$) are treated with an excess of neutral solution of sodium acetate and then titrated with silver nitrate.

Elements whose ions form colored solution with chlorine are precipitated from the solution by sodium hydroxide or potassium carbonate, and the filtrate, faintly acidified with acetic acid, is titrated as usual.

[1] Time is saved by filtering, through a dry filter paper, only a portion of the mixture made to a definite volume, and titrating an aliquot portion. The first 10–15 cc. of the filtrate are rejected.

[2] Upon addition of the ferric solution no color should develop. If a reddish or yellowish color results, more nitric acid is required to destroy this. The amount of nitric acid does not affect results when within reasonable limits.

[3] Z. anorg. Chem., **63**, 330 (1909).

[4] Depré, Analyst, **5**, 123.

Free hydrochloric acid is neutralized with ammonium hydroxide and titrated.

The accuracy of the method is seriously interfered with by high temperatures.[1] It is advisable to titrate the sample under the same conditions as those observed during standardization.

Free chlorine should be converted to a chloride before titration. This may be accomplished, as stated under preparation of the sample, by boiling with ammonium hydroxide. Free chlorine may be determined by sweeping the gas, by means of a current of air, into a solution containing potassium iodide, the liberated iodine titrated by N/10 thiosulphate, $Na_2S_2O_3$, and the equivalent chlorine estimated.

Volumetric Determination of Free Chlorine

The determination depends upon the reaction $Cl+KI=KCl+I$. The iodine liberated by the chlorine is titrated with $Na_2S_2O_3$ and the equivalent Cl calculated.

Procedure. A measured amount of the chlorine water is added to a solution of potassium iodide in a glass-stoppered bottle by means of a pipette, the delivery tip of which is just above the surface of the iodide solution. The bottle is then closed and the contents vigorously shaken. The liberated iodine is titrated with tenth-normal sodium thiosulphate ($2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$). When the yellow color of the iodine has become faint, a little starch solution is added and the titration completed to the fading out of the blue color.

One cc. N/10 $Na_2S_2O_3=0.003546$ gram Cl.

Determination of Hypochlorous Acid in the Presence of Chlorine

The determination depends upon the reactions:

$$2KI+HOCl=KCl+KOH+I_2 \text{ and } 2KI+Cl_2=2KCl+I_2.$$

The alkali liberated by hypochlorous acid and the total iodine are determined and the calculations made for each of the constituents.

Procedure. A measured volume of N/10 HCl is added to a potassium iodide solution. To this the sample containing the hypochlorous acid and chlorine are added. The liberated iodine is titrated with N/10 $Na_2S_2O_3$. (The addition of starch is omitted.) The colorless solution is treated with methyl orange indicator and the excess of hydrochloric acid is titrated with N/10 NaOH. The potassium hydroxide, produced by the action of the hypochlorous acid upon the iodide, requires half as much acid for neutralization as the volume of thiosulphate required by the iodine set free by the hypochlorous acid.

Calculation. The cc. back titration with NaOH are subtracted from the total cc. of HCl taken = cc. HCl required by NaOH liberated by HOCl = A. Then $2A$ cc. = cc. $Na_2S_2O_3$ required by the I liberated by HOCl. Cc. $A \times 0.005247$ = gram HOCl. The total $Na_2S_2O_3$ titration minus $2A$ cc. (due to the iodine liberated by HOCl) = cc. $Na_2S_2O_3$ that are required by the iodine liberated by chlorine. The cc. thus required multiplied by 0.003546 = grams chlorine in the sample taken.

[1] W. G. Young, Analyst, 18, 125.

Gravimetric Determination of Chloric Acid, $HClO_3$, or Chlorates, by Reduction to Chloride and Precipitation as Silver Chloride

Reduction of the Chlorate. Among the methods of reduction of chlorates the following deserve special mention: 1. *Reduction with Sulphurous Acid.* 2. Ferrous sulphate. 3. Zinc.

1. About 0.2 to 0.5 gram of the salt is dissolved in 100 cc. of distilled water and either SO_2 gas passed into the solution or sulphurous acid in solution added in excess. The solution is now boiled to expel SO_2 and the chloride precipitated as AgCl in presence of free nitric acid.

2. The sample in 100 cc. of distilled water is treated with 50 cc. of crystallized ferrous sulphate (10% solution), heated to boiling, with constant stirring, and then boiled for fifteen minutes. Nitric acid is added to the cooled solution until the deposited basic ferric salt is dissolved. The chloride is now precipitated as AgCl, as usual.

3. The dilute chlorate solution is treated with acetic acid until it reacts distinctly acid. An excess of powdered zinc is now added and the solution boiled for an hour. Nitric acid is added to the cooled solution in sufficient quantity to dissolve the zinc remaining. The solution is filtered, if necessary, and the chloride precipitated as usual.

Factors. $AgCl \times 0.855 = KClO_3$, or $\times 0.2474 = Cl$.

NOTE. In absence of cyanides, carbonates and acids decomposed and volatilized by hydrochloric acid, or oxides, hydroxides and substances other than chlorates that may be decomposed or acted upon by this acid, evaporation of the salt with HCl and ignition of the residue, or addition of an excess of ammonium chloride,[2] and subsequent heating will give a residue of chloride, which may be determined as usual and the equivalent chlorate calculated. Method by L. Blangey.

The methods may be used in determining chlorates in presence of perchlorates, only the former being reduced to chlorides. Outline of the procedure is given later.

Gravimetric Determination of Perchloric Acid by Reduction to Chloride

A perchlorate ignited with about four times its weight of ammonium chloride in a platinum dish may be decomposed to chloride. A second treatment is usually necessary to change the salt completely. Platinum appears to act as a catalyser, so must be added in solution if a porcelain crucible is used.

Procedure. About 0.2 to 0.5 gram of potassium perchlorate is intimately mixed with about 2 grams of ammonium chloride in a platinum crucible, the latter then covered with a watch-glass and the charge ignited gently for one and a half to two hours, the temperature being below the fusing-point of the residual chloride (otherwise the platinum would be attacked). A second addition of ammonium chloride is made and the mix again heated as before. The resulting chloride may now be determined as usual.

Factors. $AgCl \times 0.9667 = KClO_4$, $\times 0.2474 = Cl$.

[1] Blattner and Brassuer, Chem. Zeit. Rep., 1900, **24**, 793.

[2] Perchlorates are decomposed by ignition with NH_4Cl in presence of platinum.

termination of Chlorates and Perchlorates in Presence of One Another

(1) A portion of the sample is treated with about twelve times its weight of onium chloride in a platinum dish (or in a porcelain dish with the addition c. of hydroplatinic acid), and the mixture heated according to the procedure for perchloric acid (page 128). The resulting chloride is determined as This is the total chlorine in the sample.

In a second portion the chlorate is reduced by means of SO_2 or $FeSO_4$, ing to directions given for determination of chloric acid, and chlorine ined. The chlorine of this portion is subtracted from the total chlorine, erence multiplied by $3.9075 = KClO_4$. The chlorine of the second portion ed by $3.4563 = KClO_3$, or AgCl in (2) subtracted from AgCl of (1) difference multiplied by $0.9667 = KClO_4$. AgCl of (2) multiplied by $0.855 =$.

ination of Hydrochloric, Chloric, and Perchloric Acids in the Presence of One Another

otal Chlorine. If the determination is made in the valuation of niter a sample is fused with about three times its weight of alkali carbonate [1] m hydroxide,[2] in a platinum dish, whereby all the chlorine compounds erted to chlorides. If the compounds are present as alkali salts, fusion nonium chloride in a platinum dish may be made and the total chlorides ed after dissolving the residue in nitric acid.

hloride and Chlorate. If the estimation is being made in niter, 5 the salt are treated with 10 grams of zinc dust (Cl-free) in presence c. of 1% acetic acid. The solution is boiled for half an hour, filtered, chloride determined. In a mixture of alkali salts of hydrochloric, chloric, hloric acids, reduction may be accomplished by passing in SO_2 gas or g ferrous sulphate and boiling according to directions given for the ation of chlorate. The chloride now present in the residue is due to the chlorate and to the original chloride of the sample.

he chloride of the sample is determined by acidifying the salt with d (cold) and precipitating as AgCl.

lorate. The chloride and chlorate in terms of chlorine are subtracted l chlorine of (1) and multiplied by the factor for the salt desired.

ate. The chlorine of (3) is subtracted from chlorine of (2) and mul- y the factor for the compound desired.

ide. The AgCl of (3) is multiplied by the appropriate factor.

rs. $AgCl \times 0.2474 = Cl$, or $\times 0.2544 = HCl$, or $\times 0.4078 = NaCl$, or $= KCl$.

$\times 0.855 = KClO_3$, or $\times 0.9667 = KClO_4$.

$.4563 = KClO_3$, or $\times 3.9075 = KClO_4$, or $\times 2.1027 = KCl$, or $\times 3.0028 =$ or $\times 3.4535 = NaClO_4$, or $\times 1.6486 = NaCl$.

[1] Mennick, Chem. Zeit. Rep., 1898, **22**, 117.
[2] Blattner and Brasseur, Chem. Zeit. Rep., 1900, **24**, 793.

Determination of Chlorine, Bromine, and Iodine in the Presence of Each Other

The procedure is Bekk's modification of Baubigny's method.[1]

Procedure. The halogens are precipitated with an excess of silver nitrate, filtered onto asbestos or glass wool, washed, dried, and weighed as total halogens as silver salts. A second portion is precipitated and the moist, washed silver salts (0.3 to 0.4 gram) are treated with a solution of 2 grams of potassium dichromate in 30 cc. of concentrated sulphuric acid at 95° C., and digested for thirty minutes. By this procedure the iodine is oxidized to hydriodic acid (HIO_3) and chlorine together with bromine is liberated in form of the free halogen. Toward the end of the reaction a stream of air is led through the solution to remove any chlorine and bromine. This is now diluted to 300 to 400 cc., filtered, and the hydriodic acid reduced by adding, drop by drop, with constant stirring, a concentrated solution of sodium sulphite, Na_2SO_3, until a faint odor of SO_2 remains after standing ten minutes. (Under certain conditions an excess may result in a partial reduction of the silver iodide.) The precipitated silver salt is filtered, washed with hot, dilute nitric acid, dried and weighed as AgI. The filtrate containing the silver, formerly with the chlorine and bromine, is treated with potassium iodide in sufficient amount completely to precipitate the silver as AgI. This is filtered, washed and weighed. From the three weights the chlorine, bromine and iodine can be easily calculated.

NOTE. Bekk claims an accuracy within less than 0.15%.

EVALUATION OF BLEACHING POWDER, CHLORIDE OF LIME, FOR AVAILABLE CHLORINE

When chloride of lime is treated with water, it is resolved into calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$. The calcium hypochlorite constitutes the bleaching agent. The technical analysis is confined to the determination of available chlorine, which is expressed as percentage by weight of the bleaching powder.[2]

Procedure. Ten grams of the sample are washed into a mortar and ground with water, the residue allowed to settle and the supernatant liquor poured into a liter flask. The residue is repeatedly ground and extracted with water until the whole of the chloride is transferred to the flask. The combined extracts are made up to 1000 cc.

To 50-cc. portions (0.5 gram) of the solution, 3 to 4 grams of solid potassium iodide and 100 cc. of water are added and the solution acidified with acetic acid. Iodine equivalent to the available chlorine is liberated. This is titrated with N/10 arsenious acid.[3]

One cc. N/10 arsenious acid = 0.003546 gram Cl. This multiplied by 200 = %Cl.

[1] Julius Bekk, Chem. Ztg., **39**, 405–6 (1915). C. A., **9**, 2042, (1915).

[2] In France the strength is given in Gay-Lussac degrees, e.g., liters of gas evolved by 2 kilograms of bleaching powder, 0° C. and 760 mm. 100° = 31.78% Cl.

[3] The standard arsenious acid is made by dissolving 4.95 grams of pure As_2O_3 together with 20 grams of sodium bicarbonate in 50 cc. of warm water. When dissolved the solution is made up to 1 liter.

NOTE. In the analysis of compounds containing hypochlorites and chlorides, the conversion of hypochlorites to chlorides by heating with hydrogen peroxide is a great convenience.

For instances in the analysis of bleach liquors, washes, etc., the (OCl) and Cl may be very easily and quickly determined by titrating an aliquot with As_2O_3 and then a similar aliquot with $AgNO_3$ after converting all the OCl to Cl by warming with H_2O_2.

It is also a convenience in getting rid of OCl as, for instance, in the determination of CO_2 in bleaching powder, which is often of great importance. It is preferable to the use of ammonia, which is always liable to suspicion of having taken up a little CO_2, and there is no danger of NH_4Cl fumes which are sometimes a nuisance.

CHROMIUM

WILFRED W. SCOTT

Cr, *at.wt.* 52.0; *sp.gr.* 6.92; *m.p.* 1520°; *b.p.* 2200° C; *oxides*, CrO_3; Cr_2O_3, CrO_3.

DETECTION

Chromium is precipitated by hydrogen sulphide and ammonium hydroxide as bluish-green, $Cr(OH)_3$, along with the hydroxides of iron and aluminum (members of previous groups having been removed). The chromic compound is oxidized to chromate by action of chlorine, bromine, sodium peroxide, or hydrogen peroxide added to the substance containing an excess of caustic alkali. The chromate dissolves and is thus separated from iron, which remains insoluble as $Fe(OH)_3$. The alkali chromates color the solution yellow.

Barium acetate or chloride added to a neutral or slightly acetic acid solution of a chromate precipitates yellow barium chromate, $BaCrO_4$. Addition of ammonium acetate to neutralize any free inorganic acid aids the reaction.

Lead acetate produces a yellow precipitate with chromates, in neutral or acetic acid solutions.

Mercurous nitrate or silver nitrate gives red precipitates with chromates.

Hydrogen peroxide added to a chromate and heated with an acid, such as sulphuric, nitric, or hydrochloric, will form a greenish-blue colored solution. Chromates are reduced by hydrogen peroxide in acid solution, the action being reversed in alkaline solution.

Reducing agents, hydrogen sulphide, sulphurous acid, ferrous salts, alcohol form green chromic salts when added to chromates in acid solution.

Ether shaken with a chromate to which nitric acid and hydrogen peroxide are added, is colored a transient blue. Oxygen is given off as the color fades.

$$HCrO_4 + 3HNO_3 = Cr(NO_3)_3 + 2H_2O + O_2.$$

Diphenyl carbazide test. To 5 cc. of the solution containing chromium as chromate, 2 drops of hydrochloric or acetic acid are added, and 1 drop of an acetic acid solution of diphenyl carbazide (0.2 gram CO $(NH \cdot NH \cdot C_6H_5)_2$ is dissolved in 5 cc. glacial acetic acid and diluted to 20 cc. with ethyl alcohol). A violet pink color is produced in presence of a chromate. Less than 0.0000001 gram chromium may be detected.

Chromic salts are bluish green; chromic acid is red; chromates, yellow; bichromates, red; chrome alum, violet.

The powdered mineral, containing chromium, when fused with sodium carbonate and nitrate, produces a yellow colored mass.

ESTIMATION

Among the substances in which chromium is determined are the following: Chrome iron or chromite, $Cr_2O_3 \cdot FeOMgO$; crocoisite, $PbCrO_4$; slags; chromic oxide, chrome green, in pigments; chromates and dichromates; chrome steel and ferro-chrome.

Preparation and Solution of the Sample

Although powdered metallic chromium is soluble in dilute hydrochloric or sulphuric acid, it is only slightly soluble in dilute or concentrated nitric acid. It is practically insoluble in aqua regia and in concentrated sulphuric acid. Chrome iron ore is difficult to dissolve. It is important to have the material in finely powdered form to effect a rapid and complete solution of the sample. An agate mortar may be used to advantage in the final pulverizing of the substance.

General Procedures for Decomposition of Refractory Materials Containing Chromium. The following fluxes may be used:

A. Fusion with $KHSO_4$ and extraction with hot dilute HCl. The residue fused with Na_2CO_3 and $KClO_3$, 3 : 1, or fusion with soda lime and $KClO_3$, 3 : 1.

B. Fusion with $NaHSO_4$ and NaF, 2 : 1.

C. Fusion with magnesia or lime and sodium or potassium carbonates, 4 : 1.

E. Fusion with Na_2O_2, or NaOH and KNO_3, or NaOH and Na_2O_2. Nickel, iron, copper, or silver crucibles should be used for *E*. Platinum may be used for *A*, *B*, or *C*.

Special Procedures. Materials High in Silica. The finely ground sample, 1 to 5 grams, is placed in a platinum dish and mixed with 2 to 5 cc. concentrated sulphuric acid (1.84), and 10 to 50 cc. of strong hydrofluoric acid added. The solution is evaporated to small volume on the steam bath and to SO_3 fumes on the hot plate. Sodium carbonate is added in sufficient amount to react with the free acid, and then an excess of 5 to 10 grams added and the mixture heated to fusion and kept in molten condition for half an hour. From time to time a crystal of potassium nitrate is added to the center of the molten mass until 1 to 2 grams are added. (*Caution.* Platinum is attacked by KNO_3, hence avoid adding a large amount at any one time.) Chromium and aluminum go into solution in the flux, but iron is thrown out as $Fe(OH)_3$. The cooled fusion is extracted with hot water and filtered from the iron residue. Chromium is in solution together with aluminum. If much iron is present it should be dissolved in a little hydrochloric acid and the solution poured into boiling 10% solution of potassium hydroxide, the cooled solution+$Fe(OH)_3$ precipitate is treated with hydrogen peroxide or sodium peroxide to oxidize any chromium that may have been occluded by the iron in the first precipitate. The mixture is again filtered and the combined filtrates examined for chromium.

Sodium Peroxide Fusion. Chrome Iron Ores. One to two grams of finely pulverized ore are placed in a nickel or iron crucible of 50 to 75 cc. capacity and mixed with 5 to 10 grams of yellow sodium peroxide. (Fresh peroxide is best). The mass is gently heated over a Bunsen burner until it melts. The fusion is kept at a low red heat for about fifteen minutes. About 5 grams more of the Na_2O_2 are added and the fusion heated for about ten minutes more. The cooled fusion is dissolved in a casserole with 100 cc. to 150 cc. of water, more peroxide being added to this solution if it appears purple. The excess of peroxide is decomposed by boiling the solution, and to the caustic solution free from peroxide is added 10 to 15 grams of ammonium carbonate or a sufficient quantity of the salt to neutralize four-fifths of the sodium hydroxide present in the solution, as the strong caustic would otherwise dissolve the filter. The solution is now filtered. The insoluble matter is treated on the filter with dilute sulphuric

acid, 1 : 4. If a portion remains insoluble, it is an indication of incomplete decomposition of the ore, and this residue is again fused with peroxide and treated as above. The combined filtrates contain the chromium.

Since chromates are reduced in presence of free acid and peroxide, the latter should be expelled before making the solution acid.[1]

If the chromate is to be precipitated as $BaCrO_4$ or $PbCrO_4$, the solution should be acidified with hydrochloric acid. If the reduced solution is to be titrated with potassium permanganate, it is best to use sulphuric acid in neutralizing the caustic solution. Further directions will be given under the method chosen.

Method for Solution of Iron and Steel. Three to five grams of steel are boiled for about ten to fifteen minutes with 50 cc. of strong hydrochloric acid and about 150 cc. concentrated nitric acid added and the boiling continued until the hydrochloric acid is expelled, brown fumes and the odor of Cl no longer being evident. Ten grams of potassium chlorate are now added to the cooled solution, a few crystals at a time, the solution then replaced on the hot plate and boiled down to about 50 cc. to decompose the chlorate. The solution is diluted to 150 cc., and if an appreciable amount of manganese dioxide has separated out, it is decomposed by the addition of a few drops of hydrochloric acid. The chlorine is expelled by boiling and the solution cooled. Chromium is determined in this solution by the ferrous ammonium sulphate method.

SEPARATIONS

Chromium, Iron, and Aluminum. If chromium has been fused with sodium peroxide or carbonate containing a little potassium nitrate, and the fusion extracted with boiling water, most of the chromium goes into solution as a chromate, together with alumina, but some of the chromium is occluded by $Fe(OH)_3$. If the amount of the iron precipitate is appreciable, and warrants the recovery of occluded chromium, it is dissolved in hydrochloric acid and the iron reprecipitated by pouring into a solution of strong sodium hydroxide. Before filtering off the iron hydroxide, a little H_2O_2 is added to oxidize the Cr_2O_3, if accidentally present, and the solution boiled and filtered. The combined filtrates will contain all of the chromium and aluminum.

If chromium is present as a chromic salt, instead of a chromate, it is oxidized to the higher form, by adding peroxide (H_2O_2 or Na_2O_2) to the alkaline solution. Bromine added to this solution or chlorine gas passed in will accomplish complete oxidation.[2] It must be remembered that in acid solutions hydrogen peroxide, sodium peroxide, or nitrites will cause reduction of chromates to chromic salts (exception, see method for solution of steel), so that these should be boiled out of the alkaline solution before making decidedly acid with hydrochloric or sulphuric acids. Since these are difficult, if not impossible, to completely expel from an alkaline solution, after boiling the strongly alkaline solution, dilute sulphuric acid is added until the solution acquires a permanent brown color (nearly acid), acid potassium sulphate, $KHSO_4$, is added, and

[1] See Separations.

[2] Br may be added and then NaOH to oxidize Cr and precipitate $Fe(OH)_3$.

Chromic oxide and most of its compounds, except chrome iron stone, may be decomposed by conc. HNO_3+KClO_3 (added in small portions). M. Gröger, Zeitsch. anorg. Chem., 81, 233–242, 1913.

the boiling continued.[1] This will decompose the bromates and expel bromine, etc., but will not cause the reduction of the chromate, as would a strong acid solution.

Separation of Chromium from Aluminum. This separation is necessary if chromium is to be precipitated as $Cr(OH)_3$. The sodium chromate and aluminate solutions are made slightly acid with nitric acid and then faintly alkaline with ammonium hydroxide, $Al(OH)_3$ is precipitated and chromium remains in solution as a chromate.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF CHROMIUM

Precipitation of Chromic Hydroxide and Ignition to Cr_2O_3[2]

Chromium present as a chromic salt in solution, free from iron and aluminum or elements precipitated as hydroxides, is thrown out of solution by NH_4OH as $Cr(OH)_3$, the precipitate ignited to the oxide, Cr_2O_3,[3] and so weighed. The presence of hydrochloric acid or sulphuric acid does not interfere.

Reduction. If the chromium is already present as the chromic salt, free from iron and alumina, it may be precipitated directly as the hydroxide by addition of ammonia; otherwise, if present as the chromate, as is the case when a separation from iron and alumina has been necessary, and in cases where the chromium has been brought into solution by fusion with an oxidizing reagent, reduction is necessary. This is accomplished by passing SO_2 or H_2S into the slightly acid solution of the chromate, or by adding alcohol to the hydrochloric acid solution and boiling until the solution appears a deep grass green. Twenty cc. of alcohol for every 0.1 gram of Cr has been found to be ample for this reduction. The SO_2 or H_2S should be expelled from solution by boiling, in case either has been used for reduction of the chromate.

Precipitation. ***Ammonium hydroxide or ammonium sulphide are added in slight excess and the solution boiled for about ten minutes.*** The solution should be slightly alkaline (litmus), otherwise a few drops of ammonia should be added, but not a large excess; the solution will then settle out clear. A cloudy solution results from prolonged boiling when the solution has become acid; on the other hand, a large excess of ammonia will prevent complete precipitation of chromium and the filtrate will be colored pink or violet. *The chromic hydroxide is filtered off on S and S 589 filter paper.* Since the precipitate is apt to be gelatinous it is advisable to wash two or three times by decantation and several times on the paper. The well-drained precipitate and filter is ignited wet in a porcelain or platinum crucible, first over a low flame until the paper has been charred, then over a strong gas flame for about thirty minutes,

[1] $KHSO_4$ will not cause reduction of chromates. A. Kurtenacker, Zeitsch. anal. Chem., **52**, 401–407, 1913. The Analyst, **38**, 449, page 387.

[2] It is advisable to take such a weight of sample that the ignited Cr_2O_3 does not exceed 0.5 gram in weight.

[3] Cr_2O_3, *mol.wt.*, 152; *sp.gr.*, 5.04; *m.p.*, 2059°; insol. in H_2O, slightly sol. in acids, dark green hexagonal.

and finally a blast heat for five minutes. The green residue is weighed as Cr_2O_3.[1]

$$Cr_2O_3 \times 0.6846 = Cr.$$

Determination of Chromium as Barium Chromate[2]

Chromium, present as a chromate, is precipitated from a neutral or faintly acetic acid solution of an alkali chromate by addition of barium acetate or chloride. The $BaCrO_4$ is gently ignited and weighed. The solution should be free from sulphuric acid or sulphates.

Procedure. The alkali chromate solution is neutralized with nitric acid or ammonia as the case may require, precautions for avoiding reduction having been observed as indicated under Preparation and Solution of the Sample. 10 cc. of $\frac{1}{4}$ N. $BaCl_2$ or $Ba(C_2H_3O_2)_2$ (approx. 10% sol.) are added to the boiling solution for each 0.1 gram of chromium present. The reagent should be added in a fine stream or drop by drop to prevent occlusion of the reagent by the precipitate. The precipitated chromate is allowed to settle on the steam bath for two or three hours and then filtered into a weighed Gooch crucible and washed with 10% alcohol solution. The precipitate is dried for an hour in the oven, then placed in an asbestos ring suspended in a large crucible with cover and thus heated over a low flame, gradually increasing the heat until the outer crucible becomes a dull red. The cover is removed and the heating continued for five minutes, or until the precipitate appears a uniform yellow throughout. High heating should be avoided. The cooled residue is weighed as $BaCrO_4$.

$$BaCrO_4 \times 0.2055 = Cr,$$

$$BaCrO_4 \times 0.3002 = Cr_2O_3.$$

$$BaCrO_4 \times 0.7666 = K_2CrO_4.$$

$$BaCrO_4 \times 0.5807 = K_2Cr_2O_7.$$

NOTES. If the precipitate on the sides of the crucible appears green, it is ignited until the green color disappears.

If sulphates are present, $BaSO_4$ will be precipitated, hence this method could not be used. In this case either reduction to the chromic salt and precipitation of chromium as $Cr(OH)_3$ or a volumetric procedure should be followed.

Oxidize chromium with an excess of hydrogen peroxide in alkaline solution, reduce in acid solution with ferrous sulphate and titrate with permanganate. Decomposition of hydrogen peroxide is accelerated by heat and by presence of sodium sulphate or ferric salts. Salts of nickel cobalt, or manganese, decompose H_2O_2 energetically and lower results are obtained. F. Bourin and A. Senechal. Compt. rend., 157, 1528-31.

[1] If the filtrate appears yellow, chromate is indicated, the solution should be reduced and the chromium precipitated as $Cr(OH)_3$. If the filtrate is pink, it should be boiled until it appears green and $Cr(OH)_3$ precipitates. These precipitates should be included in the above calculation for chromium.

[2] $BaCrO_4$, *mol.wt.*, 253.47; *sp.gr.*, 4.498; solubility per 100 cc. H_2O, 0.00038[18°] and 0.0043 hot. Soluble in HCl and in HNO_3; yellow rhombic plates.

VOLUMETRIC METHODS FOR THE DETERMINATION OF CHROMIUM

Potassium Iodide Method for Determination of Chromium

Chromium present as a chromate is reduced in acid solution by addition of potassium iodide and the liberated iodine titrated by standard sodium thiosulphate. The method depends upon the following reactions:

$$(a)\ 2CrO_3+6KI = Cr_2O_3+3K_2O+6I.$$

$$(b)\ I_2+2Na_2S_2O_3 = 2NaI+Na_2S_4O_6.$$

The presence of large quantities of Ca, Br, Sr, Mg, Zn, Cd, Al, Ni, Co, H_2SO_4, HCl, does not interfere.[1]

Procedure. The alkali chromate solution containing not over 0.17 gram Cr [2] and free from Fe_2O_3, is made nearly acid with H_2SO_4, boiled with 20 cc. of 30% potassium acid sulphate to decompose bromates or expel Br, Cl, or H_2O_2 as the case may require, more $KHSO_4$ being added if necessary. If the solution is not acid it is made so with sulphuric acid and 5 cc. of the acid per 100 cc. of solution is added in excess.[3] About 2 grams of solid potassium iodide are added and, after five minutes, the liberated iodine is titrated with N/10 $Na_2S_2O_3$ solution. When the green color of the reduced chromate begins to predominate over the free iodine color (brownish red) a little starch solution is added and the titration with the thiosulphate continued until the blue color of the starch compound is just destroyed, care being taken not to confuse the green color of the reduced chromium with the blue of the starch.

One cc. of N/10 $Na_2S_2O_3$[4] = 0.001733 gram Cr.

Determination of Chromium by Reduction of the Chromate with Ferrous Salts

The procedure may be used for the determination of chromium in presence of ferric iron and alumina. Hydrochloric or sulphuric acids do not interfere. If hydrochloric acid is present in solution, the $K_2Cr_2O_7$ back titration should be made. In presence of H_2SO_4 either $KMnO_4$ or $K_2Cr_2O_7$ titrations may be made. The method depends upon the reduction of soluble chromates by ferrous salts, the excess being determined by titration.

Reactions. *a.* $2Cr_2O_3+6FeO+xsFeO = Cr_2O_3+3Fe_2O_3+xsFeO.$

b. *xs*FeO is oxidized by standard oxidizing reagent to Fe_2O_3.

[1] M. Gröger, Zeit. anal. Chem., 81, 233–242, 1913.

[2] If desired, stronger solution of titration reagents may be used, and consequently a larger sample taken. A normal sol. of $Na_2S_2O_3$ may be used to advantage with 1 gram samples of chromium salts or hydrates, where Cr exceeds 10%.

[3] A. Kurtenacker, Zeit. anal. Chem., **52**, 401–407. 1913.

Sutton recommends for every 0.5 gram $K_2Cr_2O_7$ present to add .5 gram KI and 1.8 gram H_2SO_4 per 100 cc. of solution. If more $K_2Cr_2O_7$ is present, increase the KI and H_2SO_4, but not the water.

[4] If desired, a normal solution of thio sulphate may be used with one gram sample of chromium salts or hydroxides, when the chromium present exceeds 10 per cent.

Procedure. *Reduction.* The sample, containing not over 0.17 gram chromium present as a chromate, is boiled to expel oxidizing reagents according to the method described under the potassium iodide procedure for chromium. The solution is made acid, if not already so, and about 5 cc. conc. H_2SO_4 per 100 cc. of solution, added in excess. Tenth normal ferrous ammonium sulphate solution containing free sulphuric acid is added until the solution changes from yellow through olive green to deep grass green. For every 0.1 gram of chromium about 65 to 70 cc. of N/10 ferrous salt solution should be added. After five minutes, the excess of this reducing reagent is titrated either with permanganate or with dichromate as directed below.

Potassium Permanganate Titration. To be used in presence of free sulphuric acid, free hydrochloric acid being absent.

Tenth-normal potassium permanganate solution is run into the reduced chromate until the green color gives place to a violet tinge. At the end-point the solution appears to darken slightly. A little practice enables one to get this with accuracy. A slight excess of permanganate gives the solution a pinkish color, readily distinguishable in the green. Addition of 3 to 4 cc. syrupy phosphoric acid gives a sharper end-point. The color should hold one minute.

Potassium Dichromate Titration. N/10 $K_2Cr_2O_7$[1] is run into the solution until a drop of the sample placed on a white glazed surface with a drop of potassium ferricyanide reagent no longer gives a blue color.

Calculation. From the total ferrous ammonium sulphate added, subtract the cc. of back titration (the reagents being exactly N/10), the difference gives the cc. of ferrous salt required for chromium reduction. If reagents are not N/10, multiply cc. titrations by factor converting to N/10.

Cc. ferrous ammonium sulphate $\times 0.001733 = Cr$.

$Cr_2O_3 + 3O = Cr_2O_6$. $\therefore Cr = 1\frac{1}{2}O$ or $= 3H$; hence $\frac{1}{3}$ mol. wt. Cr per liter = N sol.

Determination of Small Amounts of Chromium[2]

Advantage may be taken of the color produced by chromates in solution in determining small amounts, the depth of color depending upon the amount of chromate in solution. The method possesses the usual disadvantage of colorimetric procedures in that there is always room for doubt as to whether the element sought is entirely responsible for the color of the solution.

Procedure. The solution containing the sample is nearly neutralized with sodium carbonate, the reagent being added until a slight cloudiness results. The solution is now cleared with a few drops of sulphuric acid, and then sufficient excess of a strong solution of sodium thiosulphate added to precipitate aluminum, chromium, manganese, etc. The precipitate is filtered off, dissolved in the least amount of dilute nitric acid, then filtered from the precipitated sulphur and diluted to 300 to 400 cc. Chromium is now oxidized by adding 10 cc. of 0.2% silver nitrate solution, about 10 grams each of ammonium nitrate and persulphate. After boiling for about twenty minutes, sufficient hydrochloric acid is added to decompose any permanganate present and to precip-

[1] If desired, a larger sample may be taken and N/5 or N solutions used in titration. It is advisable to titrate chromium salts, e.g., over 1.0% Cr, with normal solutions, so that one gram sample may be taken for analysis.

[2] M. Dittrich, Zeitsch. anorg. Chem., 80, 171–174, 1913.

itate the silver, and a few cc. added in excess. The solution is again boiled for about ten minutes and then filtered. The filtrate is treated with a little sodium phosphate to repress the color of traces of iron that may be present and made to a definite volume.

The solution may now be compared with a standard solution containing the same amounts of acids, manganese, alumina, etc., as are present in the sample, tenth normal potassium dichromate being run into this standard solution until its color matches that of the sample. The burette reading is taken and the chromium calculated.

One cc. of N/10 $K_2Cr_2O_7 = 0.00173$ gram Cr.

NOTES. Prolonged boiling after addition of hydrochloric acid to the solution of the chromate will cause its reduction. A green tint usually indicates that the chromate has been reduced.

The test may be carried on in the presence of sulphuric, hydrochloric, phosphoric hydrofluoric, and nitric acids. Alumina, manganese, and small amounts of iron do not interfere.

Organic matter should be destroyed by either calcining the sample or by oxidation by taking to fumes with sulphuric acid. The presence of this prevents precipitation of chromium.

COBALT

W. L. SAVELL[1]

Co, *at.wt.* 58.97; *sp.gr.* 8.7918; *m.p.* 1478°; *b.p. unknown*; *Oxides*, Co_2O_3, CoO, CoO_2.

DETECTION

After the removal of the elements precipitated by hydrogen sulphide from acid solution, a little nitric acid is added to the solution to oxidize to the ferric state any ferrous salts which may be present, and ammonia is added until its odor is distinctly perceptible, to precipitate iron, aluminum and chromium.[2] This precipitate is removed by filtration and hydrogen sulphide passed through the ammoniacal solution to precipitate cobalt, nickel, manganese and zinc. After collecting this precipitate it is washed thoroughly with cold hydrochloric acid of approximately 1.035 specific gravity, to remove manganese and zinc. A small quantity of the residue is fused with borax in the loop of a platinum wire. A blue color in the cold bead indicates cobalt. This test is masked in the presence of large quantities of nickel. In this case the residue is dissolved in hydrochloric acid to which a few drops of nitric acid have been added and the solution evaporated to dryness. The residue is redissolved in water, acidified with hydrochloric acid and the cobalt precipitated with a hot solution of nitroso-beta-naphthol in 50% acetic acid. A brick red precipitate indicates cobalt.

Potassium sulphocyanate, KCNS, produces a red color with cobalt. Alcohol and ether are added to this solution and shaken. The ether layer is colored blue by cobalt. If iron is present a solution of sodium thio-sulphate, $Na_2S_2O_3$, is added until the red color disappears, the solution filtered and then treated with the alcohol-ether mixture.

Potassium Nitrite, KNO_2, added to a neutral or slightly acid solution containing acetic acid, will precipitate cobalt as a yellow complex nitrite having the formula $K_3Co(NO_2)_6$.

A solution of *dicyandiamidine sulphate* and sodium hydroxide added to a cobalt solution to which ammonia has been added until the odor is distinctly discernible, and containing from 10 to 20 cc. of 10% sugar solution, will change the color of the solution to red or reddish violet. If large quantities of nickel are present the color will be yellow or reddish yellow, after which the nickel will separate out in brilliant crystals, leaving the cobalt in solution, coloring it as described above.

A concentrated solution of *ammonium sulphocyanate* added to a cobaltous solution colors it blue. On dilution this becomes pink. Amyl alcohol or a mixture of amyl alcohol and ether 1 : 1, added to this and shaken, extracts this blue compound. Iron sulphocyanate, $Fe(CNS)_3$, likewise colors the ether-

[1] Research Chemist, Doloro Mining and Reduction Company, Doloro, Ontario.

[2] If a relatively large amount of iron is present the basic acetate method of separation is necessary, as iron occludes cobalt.

alcohol extract red, which may mask the cobalt blue. By addition of sodium carbonate solution ferric hydroxide precipitates, while the cobalt color will remain after this treatment.

ESTIMATION

Cobalt is usually estimated as metal; either reduced by hydrogen from the ignited oxide or reduced by electrolysis from an ammoniacal solution of its salts. Sometimes, however, it is estimated as oxide; usually as Co_3O_4. The reduction of the oxide by hydrogen may be carried out in conjunction with any process giving an oxide, hydroxide, carbonate, nitrate, chloride or an organic compound, as a final product.

The reduction of the metal, in solution, by electrolysis, must be accomplished in a strongly ammoniacal solution free from copper and nickel, as these metals are deposited with the cobalt on the cathode. When desirable the copper and nickel may be estimated after the electrolysis by dissolving the deposit from the cathode and proceeding in the usual manner.

Preparation and Solution of the Sample

General Procedure for Ores. The ores containing cobalt vary so widely in their chemical nature that it is difficult to lay down a method for treating all ores. However, as the principal ores contain the cobalt as a sulphide or arsenide the same general methods may be used in the majority of cases. In all cases it is necessary to prepare the sample for treatment by grinding finely. Usually either of the above ores may be brought into solution by heating with strong nitric acid or a mixture of nitric and hydrochloric acids, except silver-bearing ores, which may usually be dissolved in a mixture of nitric and sulphuric acids.

While it is desirable to use no more acid than is necessary to bring the sample into solution, an excess will not interfere, as it may be driven off by evaporation and in the event of determining the cobalt electrolytically it is essential that the solution be free from nitric acid, so that this evaporation becomes part of the procedure.

In the case of especially refractory ores or oxides of cobalt or nickel, a fusion with potassium bisulphate will usually be found sufficient as a preliminary treatment to enable it to be brought into solution. Under certain conditions, however, it has been found necessary to fuse the ore with sodium peroxide in a silver crucible, dissolving the cobalt oxide formed in hydrochloric acid. In somewhat less refractory ores of a silicious nature a preliminary fusion with a mixture of sodium carbonate and potassium carbonate with subsequent solution in hydrochloric acid or sulphuric acid, if the ore is a silver-bearing one, will be found satisfactory.

Cobalt Oxides. Cobalt oxide, gray or black, may be fused with potassium bisulphate, and the melt leached with water; or they may be treated with sulphuric acid, in which they dissolve slowly; or with hydrochloric acid, in which they dissolve more rapidly.

Metallic Cobalt, Nickel and Cobalt Alloys. Metallic cobalt dissolves readily in nitric acid, as do nickel and the ordinary cobalt alloys. There are some alloys of cobalt, however, which require fusion with sodium peroxide before they become amenable to further treatment. Among these are certain cobalt-chromium alloys.

SEPARATIONS

Separation of the Ammonium Sulphide Group Containing Cobalt from the Hydrogen Sulphide Group—Mercury, Lead, Bismuth, Copper, Cadmium Arsenic, Antimony, Tin, Gold, Molybdenum, etc.

Hydrogen sulphide passed into a hydrochloric acid solution containing from 5 to 7 cc. of concentrated hydrochloric acid per 100 cc. of solution, precipitates only the members of that group and silver, whereas the members of the subsequent groups remain in solution. If the solution is too acid, lead and cadmium are not completely precipitated.

Separation of the Ammonium Sulphide Group from the Alkaline Earths and Alkalies. Ammonium sulphide, free from carbonate, added to a neutral solution containing the above elements in the presence of ammonium chloride, precipitates only the members of this group; the alkaline earths metals, magnesium and the alkalies remain in solution. A second precipitation should be made if large quantities of the alkaline earths or alkalies are present.

Separation of Cobalt and Nickel from Manganese. The solution of the chlorides or sulphates of cobalt or nickel is treated with an excess of sodium carbonate and then made strongly acid with acetic acid. About 5 grams of sodium acetate for each gram of cobalt or nickel present is now added, the solution diluted to 200 cc. and heated to about 80° C. and saturated with hydrogen sulphide. Cobalt and nickel are precipitated as sulphides and the manganese remains in solution. The filtrate is concentrated, and colorless ammonium sulphide added when the cobalt and nickel that may have passed in solution from the hydrogen sulphide treatment, will be precipitated. The treatment should be repeated with the second filtrate to ensure complete precipitation of the cobalt and nickel.

Separation of Cobalt from Nickel. Among a number of methods for effecting this separation the following give good results:

A. Nickel is removed from the solution by precipitation with dimethylglyoxime. The details of the procedure may be found in the gravimetric methods for the determination of nickel. Cobalt remains in solution.

B. Cobalt is precipitated by nitroso-beta-naphthol, leaving nickel in solution. Details of the procedure are given under gravimetric methods for determination of cobalt.

C. Cobalt is precipitated as potassium cobalti-nitrite, nickel remaining in solution. Details of the procedure are given under gravimetric methods for the determination of cobalt.

Separation of Cobalt from Zinc. Zinc is precipitated from weak acetic or formic acid solution by hydrogen sulphide as zinc sulphide. Cobalt, nickel and manganese remain in solution. The details of the procedure are given under the methods of determination of zinc.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF COBALT

Precipitation of Cobalt by Potassium Nitrite

Cobalt may be precipitated from a solution made slightly acid with an excess of tic acid by adding a hot solution of potassium nitrite. The cobalt is precipitated potassium cobalti-nitrite, $K_3Co(NO_2)_6$, very completely, after standing for a iod of six hours in a warm place. This method has the advantage of making sible the separation of cobalt from nickel and iron, although it has the one dvantage, for commercial purposes, of requiring a long time to complete the rmination.

Procedure. After bringing the material into solution and separating the a and members of the first and second groups in the usual manner, the tion is boiled to eliminate hydrogen sulphide. Oxidize the iron present i a little hydrogen peroxide and evaporate the solution to a syrup. Take n a little water and neutralize with a practically saturated solution of sodium onate. Render slightly acid with acetic acid and add an excess of 1 : 1 ic acid. Heat to almost boiling and add solution of 50% potassium nitrite aining 100 cc. of glacial acetic acid per liter, also heated to nearly boiling. s solution should be added slowly to the solution of the sample which should agitated, preferably by rotating gently while the addition is being made. sides of the beaker should be washed down with a 1% solution of potassium ite containing 1 cc. of glacial acetic acid per liter. Allow to stand for at t six hours and if possible overnight. Filter through thick Swedish filter er without previous wetting. As this precipitate shows a very decided lency to creep, considerable care is required to keep it well down in the apex he filter-paper cone. Wash about ten times with the warm nitrite solution itioned above. Transfer to a beaker by removing the filter paper from the nel and opening it into the beaker with the outside of the paper against the s. This leaves it in a convenient position for washing. The bulk of the ipitate is washed off with 10 cc. of 1 : 1 sulphuric acid, heated to about 80° C. s should leave only a slight film of precipitate on the paper. Keep the solution he beaker at about 80° C. to assist in dissolving the precipitate and wash paper with the hot sulphuric acid solution five times, using about 10 cc. each e. Gradually withdraw the filter paper from the top of the beaker during the hing operation. Give the paper a final wash with hot water and squeeze the drops from it into the beaker. Evaporate and allow to fume strongly for minutes. Set the beaker in a cooling trough and add water until the volume bout doubled. Neutralize and make slightly ammoniacal and then add excess of 50 cc. of strong ammonia and electrolyze as described under Elecysis in Reduction of Cobalt by Electrolysis, page 144.

Precipitation of Cobalt by Nitroso-beta-Naphthol [1]

Nitroso-beta-naphthol, $C_{10}H_6(NOH)$, added to a hydrochloric acid solution of alt, precipitates cobalti-nitroso-beta-naphthol, $Co(C_{10}H_6O(NO))_3$; nickel, if ent, remains, in solution. The method is especially suitable for the deteration of small amounts of cobalt in the presence of comparatively large

[1] Burgess, Z. Angew., 1896, 596.

amounts of nickel. The cobalt precipitate is voluminous, so that the sample taken for the determination should not contain over 0.1 gram of cobalt. The reagent will also precipitate copper and iron completely from solution, also silver, bismuth, chromium and tin partially; but mercury, lead, cadmium, arsenic, antimony, aluminum, manganese, nickel, glucinum, calcium and magnesium remain in solution.

Procedure. To the solution containing the cobalt is added a freshly prepared hot solution of nitroso-beta-naphthol, in 50% acetic acid, as long as a precipitate is produced. After allowing it to settle, more of the reagent is added to insure complete precipitation of the cobalt. The compound is allowed to settle for two of three hours, the clear solution decanted through a filter and the precipitate washed by decantation with cold water, then with warm 12% hydrochloric acid solution to remove the nickel, and finally with hot water until free of acid.

The brick-red precipitate is dried, then ignited in a weighed platinum crucible (Rose crucible), first over a low flame and finally at a white heat, the crucible being covered by a platinum cover (Rose crucible type) with a platinum tube, through which is passed a slow current of oxygen. The residue is weighed as Co_3O_4. The oxide may be reduced in a current of hydrogen and weighed as metallic cobalt. Ignited in the presence of CO_2 the oxide CoO is formed.

Precipitation of Cobalt by Electrolysis [1]

Metallic cobalt is readily deposited from an ammoniacal solution of the sulphate, but in the presence of copper and nickel these are also completely precipitated on the cathode; so, in case it is desired to determine the cobalt alone it is necessary to separate these metals from the solution before electrolysis or to determine them separately after electrolysis in a solution of the metallic deposit. In practice the copper is usually separated before electrolysis and the nickel, if determined separately, is estimated afterward by one of the methods given under Nickel, the cathode deposit being dissolved for this purpose.

Procedure. After preparation and solution of the sample the usual separations with hydrogen sulphide in acid solution are made if necessary. In most cases it is necessary to pass hydrogen sulphide through the warmed solution for at least one hour to insure the complete precipitation of arsenic. Filter and boil to expel hydrogen sulphide. Add 5 cc. hydrogen peroxide to insure oxidation of iron compounds to ferric state and add ammonium hydroxide until slightly alkaline to litmus. Filter off ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. Redissolve and reprecipitate this ferric hydroxide in the above manner, using a little hydrogen peroxide in each instance, until the last traces of cobalt have been removed from it, keeping the filtrates, which should be as small as possible, to add to the main filtrate. If much iron is present this is best removed as the basic acetate.

Electrolysis. If the treatment of the iron precipitate has made a large volume of solution this may be reduced by evaporation, after which 50 cc. of strong ammonia are added and the solution electrolyzed, using direct current of 2 volts and 0.5 ampere per square decimeter. The electrodes should be platinum, the anode a spiral wire and the cathode either a hollow cylinder or a cylindrical gauze. By agitating the solution, raising the voltage and the cur-

[1] Low, "Technical Methods of Analysis."

GRAVIMETRIC METHODS FOR THE DETERMINATION OF COBALT

Precipitation of Cobalt by Potassium Nitrite

Cobalt may be precipitated from a solution made slightly acid with an excess of acetic acid by adding a hot solution of potassium nitrite. The cobalt is precipitated as potassium cobalti-nitrite, $K_3Co(NO_2)_6$, very completely, after standing for a period of six hours in a warm place. This method has the advantage of making possible the separation of cobalt from nickel and iron, although it has the one disadvantage, for commercial purposes, of requiring a long time to complete the determination.

Procedure. After bringing the material into solution and separating the silica and members of the first and second groups in the usual manner, the solution is boiled to eliminate hydrogen sulphide. Oxidize the iron present with a little hydrogen peroxide and evaporate the solution to a syrup. Take up in a little water and neutralize with a practically saturated solution of sodium carbonate. Render slightly acid with acetic acid and add an excess of 1 : 1 acetic acid. Heat to almost boiling and add solution of 50% potassium nitrite containing 100 cc. of glacial acetic acid per liter, also heated to nearly boiling. This solution should be added slowly to the solution of the sample which should be agitated, preferably by rotating gently while the addition is being made. The sides of the beaker should be washed down with a 1% solution of potassium nitrite containing 1 cc. of glacial acetic acid per liter. Allow to stand for at least six hours and if possible overnight. Filter through thick Swedish filter paper without previous wetting. As this precipitate shows a very decided tendency to creep, considerable care is required to keep it well down in the apex of the filter-paper cone. Wash about ten times with the warm nitrite solution mentioned above. Transfer to a beaker by removing the filter paper from the funnel and opening it into the beaker with the outside of the paper against the glass. This leaves it in a convenient position for washing. The bulk of the precipitate is washed off with 10 cc. of 1 : 1 sulphuric acid, heated to about 80° C. This should leave only a slight film of precipitate on the paper. Keep the solution in the beaker at about 80° C. to assist in dissolving the precipitate and wash the paper with the hot sulphuric acid solution five times, using about 10 cc. each time. Gradually withdraw the filter paper from the top of the beaker during the washing operation. Give the paper a final wash with hot water and squeeze the last drops from it into the beaker. Evaporate and allow to fume strongly for ten minutes. Set the beaker in a cooling trough and add water until the volume is about doubled. Neutralize and make slightly ammoniacal and then add an excess of 50 cc. of strong ammonia and electrolyze as described under Electrolysis in Reduction of Cobalt by Electrolysis, page 144.

Precipitation of Cobalt by Nitroso-beta-Naphthol [1]

Nitroso-beta-naphthol, $C_{10}H_6(NOH)$, added to a hydrochloric acid solution of cobalt, precipitates cobalti-nitroso-beta-naphthol, $Co(C_{10}H_6O(NO))_3$; nickel, if present, remains, in solution. The method is especially suitable for the determination of small amounts of cobalt in the presence of comparatively large

[1] Burgess, Z. Angew., 1896, 596.

amounts of nickel. The cobalt precipitate is voluminous, so that the sample taken for the determination should not contain over 0.1 gram of cobalt. The reagent will also precipitate copper and iron completely from solution, and silver, bismuth, chromium and tin partially; but mercury, lead, cadmium, arsenic, antimony, aluminum, manganese, nickel, glucinum, calcium and magnesium remain in solution.

Procedure. To the solution containing the cobalt is added a freshly prepared hot solution of nitroso-beta-naphthol, in 50% acetic acid, as long as a precipitate is produced. After allowing it to settle, more of the reagent is added to insure complete precipitation of the cobalt. The compound is allowed to settle for two of three hours, the clear solution decanted through a filter and the precipitate washed by decantation with cold water, then with warm 12% hydrochloric acid solution to remove the nickel, and finally with hot water until free of acid.

The brick-red precipitate is dried, then ignited in a weighed platinum crucible (Rose crucible), first over a low flame and finally at a white heat, the crucible being covered by a platinum cover (Rose crucible type) with a platinum tube, through which is passed a slow current of oxygen. The residue is weighed as Co_3O_4. The oxide may be reduced in a current of hydrogen and weighed as metallic cobalt. Ignited in the presence of CO_2 the oxide CoO is formed.

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Metallic cobalt is readily deposited from an ammoniacal solution of the sulphate, but in the presence of copper and nickel these are also completely precipitated on the cathode; so, in case it is desired to determine the cobalt alone it is necessary to separate these metals from the solution before electrolysis or to determine them separately after electrolysis in a solution of the metallic deposit. In practice the copper is usually separated before electrolysis and the nickel, if determined separately, is estimated afterward by one of the methods given under Nickel, the cathode deposit being dissolved for this purpose.

Procedure. After preparation and solution of the sample the usual separations with hydrogen sulphide in acid solution are made if necessary. In most cases it is necessary to pass hydrogen sulphide through the warmed solution for at least one hour to insure the complete precipitation of arsenic. Filter and boil to expel hydrogen sulphide. Add 5 cc. hydrogen peroxide to insure oxidation of iron compounds to ferric state and add ammonium hydroxide until slightly alkaline to litmus. Filter off ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. Redissolve and reprecipitate this ferric hydroxide in the above manner, using a little hydrogen peroxide in each instance, until the last traces of cobalt have been removed from it, keeping the filtrates, which should be as small as possible, to add to the main filtrate. If much iron is present this is best removed as the basic acetate.

Electrolysis. If the treatment of the iron precipitate has made a large volume of solution this may be reduced by evaporation, after which 50 cc. of strong ammonia are added and the solution electrolyzed, using direct current of 2 volts and 0.5 ampere per square decimeter. The electrodes should be platinum, the anode a spiral wire and the cathode either a hollow cylinder or a cylindrical gauze. By agitating the solution, raising the voltage and the cur-

[1] Low, "Technical Methods of Analysis."

rent density, the rate of deposition may be increased. In a properly agitated solution the deposition may be completed in forty-five minutes.

The current should not be cut off until the solution is tested to determine if the electrolysis is complete. This is done by mixing a drop or two of the solution from the end of a stirring rod with a few drops of ammonium sulphide. If the electrolysis is complete the mixture will remain colorless, but if some cobalt still remains in the solution the mixture will be darkened. After the electrolysis is complete the cathode is carefully removed from the solution and dipped into a beaker of clean water, after which it is washed with alcohol, preferably ethyl alcohol.

If a large number of electrolytic determinations are to be made, it is convenient to have a wide-mouthed bottle with a well-ground-in glass stopper or a cork stopper for holding the alcohol for the preliminary washing. The mouth should be large enough to receive the cathode without pouring out the alcohol. The cathode may be lowered into the alcohol in this bottle, which should only be partly filled, and then rinsed again by pouring fresh alcohol over it and allowing it to drain into the wide-mouth bottle. This allows a great many cathodes to be washed with a comparatively small quantity of alcohol. Directly after the final washing with alcohol the cathode is passed through the flame of a Bunsen burner and the alcohol ignited. After this is entirely burned off the cathode is placed in a desiccator to cool and when cool is weighed. The increase in weight of the cathode is the weight of cobalt in the sample if the solution had been free from nickel before electrolysis. If the nickel remained in the solution the increase in weight of the cathode represents the cobalt and nickel in the sample. If it is desired to determine the cobalt and nickel together the increase in weight of the cathode is divided by the weight of the sample and multiplied by 100 to obtain the percentage. If it is desired to obtain the percentage of cobalt separately, the plate is dissolved from the cathode in a few cc. of nitric acid and the nickel determined in the resulting solution by precipitation with dimethyl-glyoxime as described in the chapter on Nickel, after which the cobalt is found by difference.

Cobalt in Cobalt Oxide[1]

One gram of finely ground cobalt oxide is either fused with 10 grams of potassium bisulphate or heated with 20% sulphuric acid until dissolved. If the fusion method is used the melt is extracted with water and acidified with sulphuric acid. Arsenic and copper are precipitated by passing hydrogen sulphide through the warmed solution, which should be diluted to about 200 cc. for about one hour. These are removed by filtration and the cobalt determinated by one of the above methods. The following procedure is one of the most satisfactory:

Procedure. If it is desired to determine the nickel separately, as is usually the case, this is first precipitated with dimethylglyoxime as described in the chapter on Nickel, after boiling the solution to expel hydrogen sulphide. It is then evaporated to fumes of sulphur trioxide and taken up with twice its volume of water. The free acid is neutralized with ammonium hydroxide and an excess of 50 cc. of strong ammonium hydroxide added. The solution is made up to 250 cc. and electrolyzed as under Precipitation of Cobalt by Electrolysis.

[1] R. W. Landrum, Proc. Am. Ceramic Soc., **12**, 1910.

Cobalt in Steel

This determination is a modification of the nitroso-beta-naphthol method already described, as worked out in the laboratory of the Firth Stirling Steel Company, McKeesport, Pa. The procedure as described by Mr. Giles, Chief Chemist, is as follows.

Two grams of the sample are weighed into a 500-cc. Erlenmeyer flask and dissolved in 50 cc. of concentrated hydrochloric acid. When the sample is completely decomposed 10 cc. of concentrated nitric acid are added to oxidize the iron, tungsten, etc. The solution is evaporated to 10 cc.; 50 cc. of water are added; the contents of the flask are then transferred to a 500-cc. volumetric flask and cooled to room temperature. A fresh solution of zinc oxide is added in slight excess, the contents of the flask diluted to the mark, well mixed, transferred back to the original Erlenmeyer flask and allowed to settle. Filter 250 cc. (equivalent to 1 gram of the sample) through a dry filter paper, transfer it to a 500-cc. flask, then add 6 cc. of concentrated hydrochloric acid.

The solution, which should now be between 300 and 350 cc. in volume, is heated to boiling and 10 cc. of freshly prepared solution of nitroso-beta-naphthol (1 gram of salt to 10 cc. glacial acetic acid) are added for each 0.025 gram of cobalt present. Continue to heat for two minutes, remove from plate, shake well, and set aside until the bright red precipitate settles, which will only take a few minutes. Filter the hot solution and wash the flask out with hot 1 : 1 hydrochloric acid and then wash the flask out with hot acid of the same strength. Wash the paper alternately with hot (1 : 1) hydrochloric acid and hot water until it has been washed five times with the acid, then wash ten times with hot water. The precipitate is transferred to a quartz or porcelain crucible, heated gently to expel the carbonaceous matter, then at a high temperature until ignition is complete. After cooling the crucible is weighed and the weight of the residue (Co_3O_4) is multiplied by 0.734 to obtain the percentage of cobalt present. If desired the Co_3O_4 may be reduced in hydrogen and weighed as metal.

COPPER

WILFRED W. SCOTT and W. G. DERBY.

Cu, *at.wt.* 63.57; *sp.gr.* 8.89$^{20°}$; *m.p.* 1083 (*in air* 1065); *b.p.* 2310; *oxides* Cu_2O *and* CuO.

DETECTION

Copper is precipitated in an acid solution by H_2S gas, along with the other **mbers** of the hydrogen sulphide group. The insolubility of its sulphide **sodium sulphide** is a means of separating copper from arsenic, antimony, and . The sulphide dissolves in nitric acid (separation from mercury) along with **d, bismuth, and cadmium.** Lead is precipitated as $PbSO_4$ by sulphuric acid **d bismuth as the hydroxide,** $Bi(OH)_3$, upon adding ammonium hydroxide. **pper passes into the filtrate,** coloring this solution blue,

$$Cu(OH)_2 \cdot 2NH_4OH \cdot (NH_4)_2SO_4.$$

Flame Test. Substances containing copper (sulphides oxidized by roasting), **nen moistened with hydrochloric acid and heated on a platinum wire in the ame, give a blue color in the reducing flame and a green tinge to the oxidizing ame.**

Wet Tests. Nitric acid dissolves the metal or the oxides (sulphides should **e roasted),** forming a green or bluish-green solution. Ammonium hydroxide **dded to this solution will precipitate a pale blue compound, which dissolves a excess with the formation of a blue solution.** (Nickel also gives a blue color.)

Hydrogen sulphide, H_2S, passed into an acid solution containing copper, **recipitates a brownish-black sulphide,** CuS. (Distinction from nickel.)

Copper is displaced from its solution by zinc, cadmium, tin, aluminum, lead, ismuth, iron, cobalt, nickel, magnesium, and phosphorus. From a potassium **ydroxide solution it is precipitated by** K_2SnO_2. If a strip of iron is placed in a **olution of copper,** neutral or slightly acid, it will be coated over with metallic **opper. (Delicacy** 1 part Cu per 120,000 of solution.)

The greenish-blue cupric salts in acid solution are reduced to the colorless **uprous compounds by metallic copper and by stannous chloride and by rsenious acid, grape sugar,** sulphurous acid in alkaline solutions.

ESTIMATION

The estimation of copper is required in the following substances: *In ores*[1] *of copper,* in which it occurs as native copper or combined as sulphide, oxide, carbonate, chloride, and silicate. In furnace slags, mattes, concentrates, blister copper, bottoms. The determination of copper is required in the analysis of

[1] Ores, copper pyrites, yellow copper ore, $CuFeS_2$; copper glance, Cu_2S (gray to bluish-black); malachite, $CuCO_3 \cdot CuOH \cdot H_2O$ (green); azurite, $2CuCO_3 \cdot CuOH_2O$ (blue); cuprite, red copper, Cu_2O; malaconite, CuO (black); dioptase, $CuOSiO \cdot H_2O$ (green vitreous).

Cobalt in Steel

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The solution, which should now be between 300 and 350 cc. in volume, is heated to boiling and 10 cc. of freshly prepared solution of nitroso-beta-naphthol (1 gram of salt to 10 cc. glacial acetic acid) are added for each 0.025 gram of cobalt present. Continue to heat for two minutes, remove from plate, shake well, and set aside until the bright red precipitate settles, which will only take a few minutes. Filter the hot solution and wash the flask out with hot 1 : 1 hydrochloric acid and then wash the flask out with hot acid of the same strength. Wash the paper alternately with hot (1 : 1) hydrochloric acid and hot water until it has been washed five times with the acid, then wash ten times with hot water. The precipitate is transferred to a quartz or porcelain crucible, heated gently to expel the carbonaceous matter, then at a high temperature until ignition is complete. After cooling the crucible is weighed and the weight of the residue (Co_3O_4) is multiplied by 0.734 to obtain the percentage of cobalt present. If desired the Co_3O_4 may be reduced in hydrogen and weighed as metal.

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DETECTION

Copper is precipitated in an acid solution by H_2S gas, along with the other members of the hydrogen sulphide group. The insolubility of its sulphide in sodium sulphide is a means of separating copper from arsenic, antimony, and tin. The sulphide dissolves in nitric acid (separation from mercury) along with lead, bismuth, and cadmium. Lead is precipitated as $PbSO_4$ by sulphuric acid and bismuth as the hydroxide, $Bi(OH)_3$, upon adding ammonium hydroxide. Copper passes into the filtrate, coloring this solution blue,

$$Cu(OH)_2 \cdot 2NH_4OH \cdot (NH_4)_2SO_4.$$

Flame Test. Substances containing copper (sulphides oxidized by roasting), when moistened with hydrochloric acid and heated on a platinum wire in the flame, give a blue color in the reducing flame and a green tinge to the oxidizing flame.

Wet Tests. Nitric acid dissolves the metal or the oxides (sulphides should be roasted), forming a green or bluish-green solution. Ammonium hydroxide added to this solution will precipitate a pale blue compound, which dissolves in excess with the formation of a blue solution. (Nickel also gives a blue color.)

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Copper is displaced from its solution by zinc, cadmium, tin, aluminum, lead, bismuth, iron, cobalt, nickel, magnesium, and phosphorus. From a potassium hydroxide solution it is precipitated by K_2SnO_2. If a strip of iron is placed in a solution of copper, neutral or slightly acid, it will be coated over with metallic copper. (Delicacy 1 part Cu per 120,000 of solution.)

The greenish-blue cupric salts in acid solution are reduced to the colorless cuprous compounds by metallic copper and by stannous chloride and by arsenious acid, grape sugar, sulphurous acid in alkaline solutions.

ESTIMATION

The estimation of copper is required in the following substances: *In ores*[1] *of copper*, in which it occurs as native copper or combined as sulphide, oxide, carbonate, chloride, and silicate. In furnace slags, mattes, concentrates, blister copper, bottoms. The determination of copper is required in the analysis of

[1] Ores, copper pyrites, yellow copper ore, $CuFeS_2$; copper glance, Cu_2S (gray to bluish-black); malachite, $CuCO_3 \cdot CuOH \cdot H_2O$ (green); azurite, $2CuCO_3 \cdot CuOH_2O$ (blue); cuprite, red copper, Cu_2O; malaconite, CuO (black); dioptase, $CuOSiO \cdot H_2O$ (green vitreous).

alloys containing copper,[1] brass, bronze, etc. It is occasionally looked for as an undesirable impurity in food products. It is determined in salts of copper in insecticides, germicides, etc.

Preparation and Solution of the Sample

Hydrochloric and sulphuric acids are effective in dissolving metallic copper only in presence of an oxidizing agent; nitric acid is the most active solvent. The oxides of copper may be dissolved in hydrochloric or sulphuric acid, but nitric acid is commonly used.

Ores. If the ore consists practically of a single mineral, the fineness of the sample need not exceed 80 mesh. If the ore is a mixture of minerals, lean and rich in copper, the laboratory sample should pass a 120-mesh sieve.

Metallic particles or masses are separated at some stage in the process of sampling and made into a separate sample. If the metallic portion is a small percentage of the total sample and consists of particles, the value of which is known to vary by a few percent, no attempt is made to crush the sample of such, but a large portion, 10–100 grams, is taken for analysis and the copper determined in an aliquot part of the solution. If the metallic masses are a large percentage of the sample, large of size, or consisting of particles differing widely in copper content, a weighed amount of 1 to 50 lbs. is melted in a graphite crucible, with addition of suitable fluxes, such as powdered silica or lime, if necessary. Separate samples are made of the weighed products of the fusion and the copper content of the material before melting calculated from their analyses. The amount of the sample taken for analysis depends upon the richness of the ore; as a general rule 0.5 to 1 gram sample is taken of ores containing over 30% copper, 2 grams of 10 to 30% copper ores and 5 grams of ores containing less than 10% copper.

Sulphide Ores. Copper Pyrites, Copper Glance, Iron Pyrites, etc. One to five grams of the finely ground ore is dissolved in a flask by adding 10 to 20 cc. of dilute nitric acid (sp.gr. 1.2), warming gently for about fifteen minutes. The solution is evaporated to small volume and nitric acid expelled by either taking to dryness, after adding hydrochloric acid, or to SO_3 fumes, upon the addition of 5 to 10 cc. of dilute sulphuric acid, 1 : 1. In presence of lead the latter procedure is recommended.

The residue is taken up with 20 cc. of water acidulated with sulphuric acid (10%) diluted to about 150 cc. and the mixture brought to boiling. Lead sulphate, if present, is filtered off together with silica, and copper passes into the solution.

Copper may now be separated from other interfering elements by one of the procedures outlined under Separations, then determined gravimetrically or volumetrically.

NOTES. The sulphur that appears upon adding acid to the ore, with proper precautions, should be yellow. If it is dark and opaque, the solution has been overheated, and some of the ore has been occluded. It is advisable in this case to remove the globule of sulphur and oxidize it separately with bromine and nitric acid, then boil out the bromine and add the solution to the rest of the sample.

Sulphide ores may be treated according to the procedure recommended for iron pyrites in the chapter on Sulphur, the ore being decomposed with a mixture of bromine and carbon tetrachloride, 2 : 3, followed by nitric acid and then sulphuric acid.

[1] Alloys of zinc, tin and zinc, aluminum, silver, nickel, manganese, and gold.

Matte. 0.5 to 1 gram of the fine sample is dissolved in nitric acid and evaporated with sulphuric acid as in case of ores.

Oxidized Ores, Oxides, etc. The sample is dissolved in nitric acid and evaporated with dilute sulphuric acid to pastiness, and then heated to SO_3 fumes. Frequently a direct treatment with dilute sulphuric acid or with hydrochloric acid may be employed.

Treatment of Matte Slag. Only by quick quenching of the molten slag is decomposition of the sample by acids made possible, without preliminary treatment with hydrofluoric acid. As a rule lime slags are readily decomposed by mixed acids. Extremely acid, or iron slags, are apt to be refractory and are decomposed with most certainty by treatment with hydrofluoric acid followed by fusion with potassium bisulphate.

The following scheme (White—Chemist Analyst, July, 1912) of attack, which also can be applied to silicious ores, with skilful manipulation gives very satisfactory results.

One gram of the 100 mesh fine slag is placed in a 250 cc. beaker of Jena glass, moistened with water, mixed with 3 cc. of sulphuric acid (sp.gr. 1.54), and then, while the particles of the slag are in suspension through rotary movement of the beaker, 15 cc. hydrochloric acid are added. The silica is gelatinized in 2 or 3 minutes by heating the beaker over a free flame. One cc. nitric acid followed by a few drops of hydrofluoric acid are added, and the heating continued in a hood until the material is nearly dry, and then to strong sulphuric acid fumes on a hot plate. When cool, 4 cc. of sulphuric acid (sp.gr. 1.54) are added.

The remainder of the procedure depends upon the method that is to be followed in the determination of copper. If the electrolytic method is preferred, 3 cc. of nitric acid are added; the mass heated until solution is effected, the liquid diluted to 175 cc. with cold, distilled water, and copper plated out in 20–35 minutes, using a rotating anode and 2½ amperes current.

If the iodide method is to be followed, without addition of other acid than sulphuric, the mass is again heated to fumes. When cooled, 25–30 cc. water and 5 cc. hydrochloric acid are added and the liquid boiled until clear. After addition of 40 cc. saturated solution of sodium acetate, 4½% solution of sodium fluoride is added until the color of ferric acetate is discharged, and then an excess of 10 cc. When cold titration is commenced, using a thiosulphate solution with a copper equivalent of 0.0005 g. per cc.

The following quick method has been systematically and satisfactorily checked for a long period by a hydrofluoric acid-bisulphate fusion method, by which copper, precipitated as a sulphide, is ignited, the oxide dissolved in nitric acid and copper determined by electrolysis.

Three grams of the 100 mesh fine sample are placed in an 800 cc. Jena beaker. The slag is spread over the bottom of the beaker, and while in motion 5 cc. of sulphuric acid are added rapidly to prevent the slag gathering into a mass. After addition of 40 cc. hydrochloric acid, the beaker is heated over a bare flame for about 3 minutes until the silica has gelatinized. To the hot solution nitric acid is added, drop by drop, until the liquid becomes dark brown. To the liquid, while in a state of agitation, 1–2 cc. hydrofluoric acid are added and the mixture boiled until the solution is complete. The liquid is diluted to 400 cc. and saturated with hydrogen sulphide and the precipitate filtered and washed as usual. The copper sulphide is ignited in a silica crucible; the residue, if washing of the precipitate has been thorough, can be brushed into a 250 cc. beaker d in

dissolved with a few cc. of nitric acid. After boiling gently to expel nitrogen gases, the free acid is neutralized with ammonia, and the solution then acidified with a slight excess of acetic acid. The cold solution is titrated by the iodide method, using a thiosulphate solution having a copper equivalent of about 0.0005 g. per 1 cc.

Metals. A casting of a copper alloy and even of refined copper is not homogeneous, and the zones of segregation of the constituents of the alloy (usually roughly parallel to the cooling surfaces) are the more sharply defined as the conditions which favor diffusion of the eutectic prevail, therefore, unless the casting be quite thin and quickly cooled, a satisfactorily representative sample of it cannot be obtained from a single drill hole. A single casting may be sampled by complete cross-sectional cuts by a suitable saw or by a series of drill holes located in such a manner as to amount substantially to one or more cross-sectional cuts. Steel is usually present as a contaminant of the drill or saw shavings from refined copper and the tougher alloys and should be removed by a magnet. Crude copper, such as blister or black copper, is sampled by drilling one hole in each piece of a definite fraction of the total pieces of the average lot. The position of the hole in successive pieces is changed to conform with a pattern or "templet" which will cover a quarter, or half, or the complete top surface of the average piece, the "templet" is divided into squares, preferably about 1 inch on a side, and in the centre of each square the ½-inch hole is drilled. The drillings are ground to pass a 20-mesh screen and the sample then withdrawn by means of a riffle sampler.

Sampling by splashing from a molten stream and by slowly pouring the metal into water are methods frequently practiced. The size of the particles, the degree of homogeneity and the limit of accuracy of result required are factors which determine whether one or more grams of the sample should be taken for analysis.

Iron Ores and Iron Ore Briquettes. A 5-gram sample of the finely divided material is fused in a large platinum dish with 40 grams of pure potassium bisulphate. If the ore is high in sulphur, it should be roasted by heating to redness in a silica or porcelain crucible before placing in the platinum dish and mixing with the bisulphate.

The cooled fusion is broken up into small pieces and placed in an 800-cc. beaker with clock-glass cover. Three hundred cc. of hot water and 25 cc. of strong hydrochloric acid are added and the fusion is boiled until it passes into solution. If an appreciable residue remains, the solution is filtered, the residue fused with additional bisulphate, then dissolved in hot dilute acid and the filtrate added to the first solution. Silica and barium sulphate remain in the residue.

The solution is now reduced and copper precipitated according to directions given under "Separation of Copper by Precipitation in Metallic Form by a more Positive Element," aluminum powder being preferably used.

The precipitated copper is filtered free from iron and other commonly occurring impurities, then dissolved by pouring on the precipitated metal 30 cc. of hot dilute nitric acid, 1 : 1, followed by 10 cc. of bromine water and then 10 cc. of hot water. The filter paper is removed, ignited and the ash added to the copper solution. The whole solution is now evaporated to small volume and determined, preferably, by the "Potassium Iodide" method as described under the volumetric procedures.

Steel, Cast Iron, and Alloy Steels.[1] From 3 to 5 grams of steel, depending upon the amount of copper present, are dissolved in a mixture of 60 cc. of water and 7 cc. of sulphuric acid (sp.gr. 1.84) in a 250-cc. beaker. After all action has ceased, a strip of sheet aluminum, 1½ ins. square, bent so that it will stand upright in the beaker, is placed in the solution.

After boiling the solution for twenty to twenty-five minutes, which is sufficient to precipitate all of the copper in the sample, the beaker is removed from the heat and the cover and the sides washed down with cold water. The liquid is decanted through an 11-cm. filter, the precipitate washed three times with water, then placed with the filter in a 100-cc. beaker, and 8 cc. of concentrated nitric acid and 15 cc. of water are poured over the aluminum and the solution heated to boiling. This hot solution is poured over the precipitate and filter in the 100-cc. beaker, and boiled until the paper becomes a fine pulp, only a few minutes being required. The solution is filtered, the residue washed several times with hot water and the filtrate and washings, not over 200 cc., are received in an electrolytic beaker, 2 cc. of concentrated sulphuric acid added and the solution electrolyzed, using a current of 2 amperes with an E.M.F. of 2 volts. With gauze cathodes and anodes the deposition is complete in an hour and a half.

SEPARATIONS

Isolation of copper in presence of large amounts of iron, or in substances containing nickel, cobalt, zinc, bismuth, cadmium, etc., may be accomplished by precipitation of the element as cuprous sulphocyanate according to the following procedure:

Precipitation of Copper as Sulphocyanate. Nitric acid having been expelled from the sample, the solution, 50–100 cc., is nearly neutralized with sodium carbonate and the copper reduced by addition of sodium bisulphite or metabisulphite or by passing in SO_2 gas. The solution is gently warmed and potassium sulphocyanate reagent added (50 grams KCNS salt per liter), until no further precipitation takes place. The sulphocyanate solution may be prepared by addition of 50 grams of potassium bisulphite or metabisulphite to the above reagent. The preliminary reduction of copper is then unnecessary, as reduction takes place with addition of the reagent. After settling, the precipitate is collected on a filter and washed free of acid, first washing with the precipitating reagent, then with ammonium acetate solution and finally with water.

The precipitate may now be dissolved in nitric acid and evaporated to near dryness with sulphuric acid and copper determined by electrolysis or by potassium iodide procedure.

The precipitated cuprous sulphocyanate may be weighed after drying at 100° C., the compound having been collected in a weighed Gooch crucible. The compound multiplied by 0.5226 gives the equivalent metallic copper.

The precipitate may be dried and burned with sulphur and the residue weighed as cuprous sulphide, Cu_2S. This multiplied by 0.7986 gives the equivalent weight of copper.

Reaction. $2CuSO_4+2KCNS+SO_2+2H_2O=2CuCNS+2H_2SO_4+K_2SO_4$.

[1] W. B. Price, Jour. Ind. Eng. Chem., Vol. 6, No. 9, p. 170.

NOTE. Cuprous sulphocyanate is insoluble in water and in dilute hydrochloric acid. With the exception of silver, selenium and tellurium copper is the only metal that is precipitated in hydrochloric acid solution by potassium sulphocyanate, hence it may be separated from other elements that would interfere in its determination by this method.

Separation of Copper by Precipitation in Metallic Form by a More Positive Element. Metallic aluminum or zinc is more commonly used in this procedure. A strip of pure aluminum or zinc, placed in the neutral or slightly acid solution, causes the complete deposition of copper. The copper is removed mechanically from the displacing metal and dissolved in nitric acid and then estimated, or the aluminum may be dissolved with the copper.

A method of precipitation by means of powdered aluminum is recommended especially for separation of copper from large amounts of iron, iron ores and iron ore briquettes. The solution of the bisulphate fusion of the iron ore is heated until bubbles appear over the bottom of the containing beaker. Aluminum powder is now added in small portions at a time, in sufficient quantity to reduce the iron, the solution becoming colorless. The solution is now heated until the aluminum completely dissolves. Metallic copper is precipitated. It is advisable to add 25 cc. of water saturated with H_2S gas to precipitate traces of copper in solution. The solution is filtered while hot through a filter (S. & S. No. 589), and washed six times, keeping the residue covered with water to prevent oxidation by air. The copper is now dissolved in hot dilute nitric acid, evaporated to small volume and determined by the procedure preferred. The potassium iodide method gives excellent results.

Separation of Copper from Members of the Ammonium Sulphide and Subsequent Groups by Precipitation as Copper Sulphide in Acid Solution. The solution containing free hydrochloric or sulphuric acid is saturated with H_2S gas,[1] the precipitated copper sulphide (together with the members of the group), is filtered and washed, first with water containing H_2S and finally with a little pure water. The residue is dissolved in nitric acid and the resulting solution examined for copper.

Removal of Silver. This element is precipitated as the insoluble chloride, AgCl, by addition of hydrochloric acid, and may be removed by filtration, copper passing into the filtrate.

Removal of Bismuth. Upon adding ammonium hydroxide to a solution containing copper and bismuth the latter is precipitated as $Bi(OH)_3$ and may be removed by filtration. Copper passes into the filtrate as the double ammonium salt. Ammonium carbonate or potassium cyanide may be used instead of ammonium hydroxide.

Removal of Lead. Lead is precipitated by sulphuric acid as $PbSO_4$ and may be removed by filtration, copper passing into the filtrate.

Removal of Mercury. The sulphide of mercury remains undissolved when the precipitated sulphides are treated with dilute nitric acid, copper sulphide dissolving readily.

Removal of Arsenic, Antimony, and Tin. These elements may be removed by dissolving their sulphides with a mixture of sodium sulphide and sodium hydroxide. Copper sulphide remains insoluble.

[1] Copper may be precipitated as the sulphide by nearly neutralizing the free acid with sodium hydroxide, warming the solution and adding crystals of sodium thiosulphate. Upon boiling black sulphide of copper is precipitated together with free sulphur.

In an alloy tin and antimony may be precipitated as oxides by evaporation of the solution of the alloy with strong nitric acid, copper remains in readily soluble form.

Separation from Cadmium. The sulphides in a solution of dilute sulphuric acid, 1 : 4, are boiled and H_2S gas passed in for twenty minutes, the solution being kept at boiling temperature. Cadmium sulphide dissolves while copper sulphide remains unaffected. The solution is filtered hot, the air above the filter being displaced by CO_2 to prevent oxidation. Traces of cadmium are removed by repeating the operation. (Method by A. W. Hofmann.)

GRAVIMETRIC DETERMINATIONS OF COPPER

Deposition of Metallic Copper by Electrolysis

The electrolytic method of determining copper is the most accurate of the gravimetric methods. This deposition may conveniently be made from acid solutions containing free nitric or sulphuric acid) or from an ammoniacal solution.

Fig. 27.—Terminal Case Showing Battery of Electrodes for Electrolytic Deposition of Copper.

The end sought by this method is to plate out all, except a trace, of the copper in the form of an evenly distributed, firmly adherent, very finely crystalline deposit, which is free from a weighable amount of impurity.

In ores, mattes, alloys (from which lead has been removed as the sulphate by taking the solution to fumes with sulphuric acid) deposition by electrolysis, from a solution containing free sulphuric acid, is convenient. On the other hand, deposition from a nitric acid solution is advantageous under conditions where this reagent has been used as a solvent and evaporation with sulphuric acid is unnecessary. This is the case in the analysis of certain alloys and the determination of copper from which impurities have been largely removed. Deposition from an ammoniacal solution is recommended when the copper salt contains chlorides and it is desired to avoid evaporation with sulphuric acid. A chloride in an acid solution gives rise to a spongy deposit of copper, and endangers a solvent action on the anode and deposition of platinum on the cathode.

Conditions other than the presence of precipitable impurities, which affect the character of the deposit are—quantity and concentration of copper, size and shape of electrodes, current density, uniformity of distribution of current to the cathode, volume, temperature and rate of circulation of the electrolyte, and concentration of oxidizing agents such as nitric acid and ferric salts. Inasmuch as the change of one condition limits or makes possible or necessary a modification of others, a large number of practicable combinations of conditions are possible. For discussion of these conditions reference is made to articles by Blasdale and Cruess, Jour. Am. Chem. Soc. Oct. 1910, 1264; and by Richards and Bisbee, Jour. Am. Chem. Soc., May, 1904, 530.

By the feature of rate of deposition, electrolytic methods may be classified as "slow" or "rapid." The slow methods, with 12 to 24 hour periods of electrolysis, are practiced when extreme accuracy is required, or when the distribution of laboratory labor and time allowed for completion of the assays permit their economical employment. The electrolyte is a solution of sulphate salts of the metals present, ammonium sulphate or nitrate, and a quantity of free nitric acid, which varies with the amount of copper and ferric salts present, and the current density employed. The oxidizing effect of nitric acid is intensified by the presence of ferric ions.[1] Electrolysis is carried out at room temperature, at current densities varying from ND/100, 0.15 to 0.5 amperes; and deposition on plain, corrugated, slit or perforated platinum cylinders from 0.75 to 2 in. diameter having 50 to 200 cm. depositing surface. A perforated cylinder permits freedom of circulation between the two surfaces of the electrode, the most even distribution of current density, and produces the most uniform coating of the foil. On account of the effect on the character of the deposit by oxygen lodging in regions of the cathode where the current density and circulation is least, the anode should be of such a form that all the gas liberated will be in the zone of maximum circulation. To procure uniform behavior under given conditions the size and shape of the electrolytic beaker should be such as to present the smallest practicable volume of electrolyte between the outer surface of the cylinder and the inside of the beaker. An unclosed seam or rivetted joint in a negative electrode will hold tenaciously salts which require extreme care to remove. It is probable that such recesses retain traces of the electrolyte underneath the coating of copper.

Rapid methods have a tendency to procure high results, resolution and mechanical loss through misting having been prevented. Deposition is hastened by increasing the rate of circulation and the current density. Circulation is

[1] Larison, Eng. and Min. Jour. 84, 442. Fairlie and Boone, Elect. and Met. Ind. 6, 58.)

promoted by the use of the gauze cathode,[1] by rotating either cathode,[2] or by placing the vessel, containing the solution and electrodes, in a field of electromotive force.[3] Quick deposition of a quality satisfactory for some classes of work is brought about by increase of current density upon an electrolyte heated to 50° to 80° C. In all the quick methods, the progress of electrolysis should be watched, and the cathode removed as soon as completion of deposition is detected by the evolution of gas about its surface. The completion of action is ascertained with greater certainty by addition of water to the electrolyte and observing whether the newly exposed surface of the cathode remains bright. When the electrolyte is hot or has a high acid content, detachment of the cathode should be preceded by removal of the electrolyte and simultaneously washing the cathode without interruption of the current. A syphon may be employed, water being added as the liquid drains from the beaker until the acid is removed.

RAPID METHODS

Rapid Deposition of Copper—Solenoid Method of Heath[4]

The solenoid is made by winding 500 turns of No. 13 B and S gauge magnet wire upon a copper cylinder $2\frac{3}{4}$ in. in diameter, $3\frac{1}{4}$ in. high, $\frac{3}{32}$ in. thickness of metal. The cylinder is brazed water tight at the bottom to a $5\frac{1}{2}$ in. disc of $\frac{3}{32}$ in. soft steel. In this disc is a 1-in. hole for the insertion of a rubber plug, through which glass tubes may be inserted for inlet and outlet of air or water to cool the electrolytic beaker. A steel disc of the same size as the bottom and with an opening to fit is brazed to the top of the cylinder. The solenoid thus made is suitable for a 300 cc. lipless beaker $4\frac{1}{4}$ in. high and $2\frac{1}{4}$ in. diameter. The solenoid coil may be in series in the electrolytic line or excited separately.

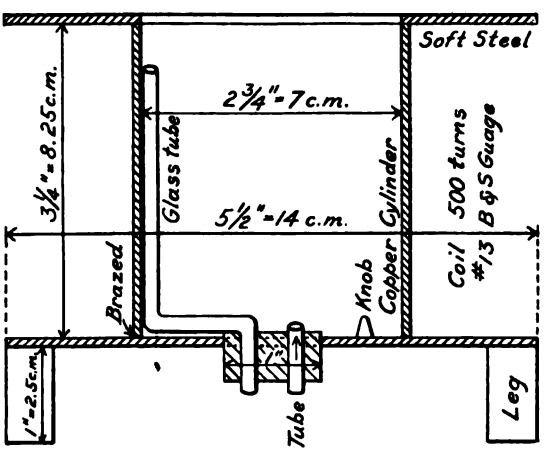

FIG. 28.

The negative electrode is of gauze 40 meshes per linear inch, with a depositing surface of 100 cm. and is slit to permit quick removal from the electrolyte.

[1] Stoddard, Jour. Am. Chem. Soc., 1909, 385. Price and Humphreys, Jour. Soc. Chem. Ind., 1910, 307.

[2] Eng. and Min. Jour., 89, 89, 1910.

[3] Frary, Jour. Am. Chem. Soc., Nov., 1907, 1592. Heath, Jour. Ind. Eng. Chem., Feb., 1911, 74.

[4] Heath, Jour. Ind. Eng. Chem., Feb., 1911, 76.

Procedure. Five grams of the thoroughly cleaned copper sample are dissolved in the covered electrolytic beaker on a steam plate with 40 cc. of stock acid solution composed of 7 parts (1.42 sp.gr.) nitric acid, 10 parts sulphuric acid (1.84 sp.gr.) and 25 parts by volume of water. The temperature during the solution is kept just below the boiling point, 50 cc. of the stock solution is used for copper containing 0.03 to 0.1 per cent of arsenic, 60 cc. for material containing 0.11 to 0.5 per cent arsenic. The electrolyte is diluted to 120 cc. A current of 4.5 amperes is used for the electrolysis and the same amount employed to excite the solenoid. During the deposition a double pair of watch glasses cover tightly the beaker until the color of the electrolyte fades out, when they are rinsed and removed. In about 30 minutes a test for completion of deposition is made by withdrawal of 1 cc. onto a porcelain tile and treating with a few drops of freshly prepared hydrogen sulphide water. This test will detect the presence of 0.000005 g. copper or more remaining in the solution. The determination is complete in two and a half hours.

NOTES. The advantage of the solenoid over any mechanical device for the rotation of electrodes is due to the prevention of loss by spraying from the anode, as the beaker can be covered with a double pair of watch glasses.

Results range from 0.003 to 0.01 per cent higher than the author's slow method of assay of refined copper, and is due to platinum from the anode, which is corroded by the influence of heat, nascent nitrous acid and high current.

Deposition from Nitric Acid Solution. The solution should not contain over 2–3 cc. of free concentrated nitric acid. If more than this is present, the solution is evaporated to expel most of the acid, the remainder neutralized with ammonia and the requisite amount of nitric acid added. The solution is diluted to 100 cc., warmed to 50° or 60° C. and electrolyzed with a current of 1 ampere and 2–2.5 volts. Two hours are sufficient to deposit 0.3 gram copper. Since nitric acid acts vigorously on copper, it is necessary to wash out the acid from the beaker before breaking the current. (See method for copper in alloys, page 174.)

Deposition from an Ammoniacal Solution. Ammonium hydroxide is added to the solution containing copper until the precipitate, first formed, dissolves. Twenty to twenty-five cc. of ammonium hydroxide (sp.gr. 0.96) are required for 0.5 gram copper or 30-35 cc. for 1 gram. Three to four grams of ammonium nitrate are added and the solution electrolyzed with a current of $ND/100 = 2$ amperes. The electrodes are washed, without breaking the current, until the ammonia and nitrate are removed.

Lead, bismuth, mercury, cadmium, zinc and nickel should be absent from the ammoniacal solution. Arsenic is not deposited. Unless a very pure platinum anode is used, platinum may contaminate the deposit appreciably. Jena or other brand of zinc borate resistance glass should not be used for the electrolytic beaker.

SLOW METHODS

Electrolytic Determination of Copper in Blister Copper

The sample should be no coarser than 20 mesh. Because fine particles are comparatively poor in copper, extreme care must be taken in drawing the portion for analysis to preserve the ratio of the coarse to fine. Some analysts, to avoid sampling error, sieve the coarse from the 40 or 60 mesh fine and either make a separate analysis of each weighed product, or weigh into a single test the due proportion of each. Others draw a large portion, by means of a riffle

(Fig. 30) or similar sampling device and from its solution in a volumetric flask, pipette an aliquot part equivalent to one or more grams.

By the small portion method insoluble matter must be removed by filtration. When the sample contains an insignificant quantity of insoluble matter, the practice is to deposit the silver with the copper and make a correction for its presence in accordance with the result of the silver assay of the sample.

By the large portion method, insoluble matter and silver, as silver chloride, is removed from the electrolyte by sedimentation in the volumetric flask.

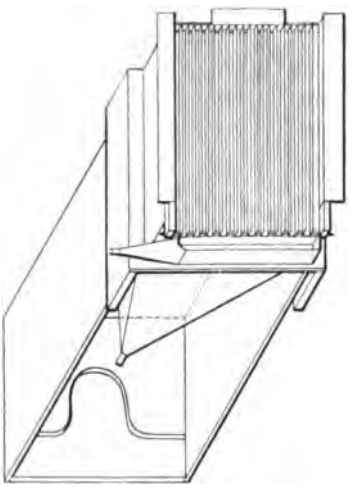

FIG. 29.—Riffle Sampler.

Procedure. Small Portion Method. The coarse and fine portions are quartered down to convenient amounts and from these a 5 gram composite weighed, which contains the coarse and fine portions in ratio of their percentage weights. The sample is placed in a 350 cc. tall form beaker, without lip and with flaring rim. Fifty cc. of chlorine free, stock acid solution (15 parts nitric and 5 parts sulphuric acids) are added, the beaker covered with a funnel (stem up), which just fits in the rim, and the mixture heated gently at first and finally to boiling. When the sample has dissolved, 5 cc. saturated solution of ammonium nitrate are added and the sample diluted to 200 cc. with water.

When the electrolyte has cooled to room temperature the electrodes are introduced, the beaker covered with split watch glasses and electrolysis started with a current of .05 ampere and continued until the appearance of the foil indicates that the silver has deposited. The current is then raised to ND/100 = .75 ampere and this continued for twenty to twenty-two hours, or until the appearance of gas about the negative electrode indicates that deposition of the copper is practically complete. For the unexperienced a simple method is to add a little water to the electrolyte without breaking the current and after 15 minutes to observe whether any deposition or copper takes place on the freshly exposed surface. The watch glasses and electrode stems should be rinsed when the electrolysis has continued 15–16 hours.

Procedure. Large Portion Method.[1] The sample is quartered by a riffle sampler (see Fig. 29) to an amount very close to 50 grams. This quantity is weighed and transferred by a paper chute into a 2000 cc. flask, which has been calibrated by the method of repeated delivery at constant temperature, of a 50 cc. overflow, dividing pipette (see Fig. 30). The liquid employed in calibrating is a copper solution of the same composition as that for which the flask is to be used. A cold mixture of 80 cc. sulphuric acid (sp.gr. 1.82) and 200 cc. nitric acid (1.42) with 500 cc. of water is added. A standard solution of sodium chloride is added in sufficient quantity to precipitate the silver, care being taken to add less than 20% excess. A bulbed condenser tube is placed in the neck before putting the flask on a hot plate.

The solution is gradually heated to boiling and when the solution is nearly complete, boiled gently for one hour. This generally completely dissolves the

[1] W. C. Ferguson, Jour. Ind. and Eng. Chem., May, 1910.

copper present. Residues of lead, tin, silver, or silica if present in appreciable amounts are separated at this point by filtration.

When the solution in the flask has cooled for half an hour, water is added to a little above the 2000-cc. mark, giving the flask a rotary motion, during the addition, to mix the solution. The flask is placed in a large tank, Fig. 30,

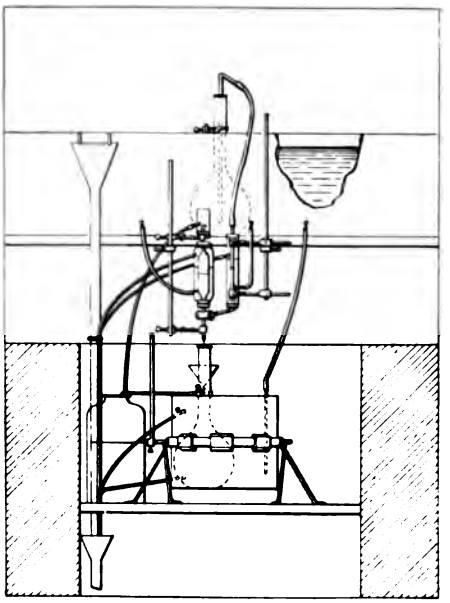

FIG. 30.—Constant Temperature Bath and Dividing Pipette.

containing water and allowed to remain until it becomes of the same temperature as the water and very close to that of the room. The solution is then made exactly to the mark and allowed to settle, after thorough mixing, by placing the flask again in the water tank.

Electrolysis. Portions equivalent to 2 grams of sample are measured out by means of a dividing pipette, with water-jacket through which the tank-water flows. The solution is run into glasses, hydrometer-jar in shape, with concave bottoms, height of glass, 6½ ins., diameter 2⅛ ins., Fig. 31. Each portion is treated with 5 cc. of a saturated solution of ammonium nitrate and diluted to 125 cc. with water. (NH_4NO_3 or $(NH_4)_2SO_4$ delays deposition of As and Sb until electrolyte is freed from Cu.) The electrolyte, at this stage, contains about 3.7 cc. of nitric acid.

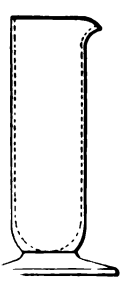

FIG. 31.

The copper is deposited by electrolysis, using a current of .33 ampere per 100 sq.cm., which is kept constant until deposition is complete, about twenty hours. It is advisable to begin the electrolysis in the evening, 5 P.M. The following morning, the inside of the jar, the rods of the electrodes, and the split watch-glasses which cover the jar are rinsed with a spray of water into the glass and the run continued for two or three hours. Each electrode is quickly

detached from the binding posts, the cathode plunged into cold water, then successively into three jars of 95% alcohol, shaken free of adherent drops and dried by revolving rapidly over a Bunsen flame for a few seconds, after ignition of the film of alcohol.

The weighing of foil plus the deposit is made with as little delay as possible.

Determination of the Copper Remaining in the Electrolytes. The electrolyte is concentrated and any residual copper precipitated as sulphide by H_2S after first neutralizing the free acid and then making slightly acid with HCl. The copper sulphide is dissolved with a little hot HNO_3 and made ammoniacal. The color of the solution is compared with a standard solution treated with the same amount of reagents as the sample, care being taken that similar conditions prevail when making comparison. The electrolytes seldom contain over 0.01% copper.

Notes and Precautions

Character of the Deposits. The ideal deposit is of a salmon-pink color, silky in texture and luster, smooth and tightly adherent. A slightly spongy and coarsely crystalline deposit, although good in color and perfectly adherent, will invariably give high results. A loosely adherent deposit caused by either too rapid a deposition at the commencement or too low a current density at some period of the electrolysis, usually shows a red tint and may give a high result on account of oxidation or a low result because of detachment of particles. A darkly shaded deposit indicates the presence of impurity in greater or less extent. If it is impossible to complete the electrolysis without this appearance the electrolyte should be purified. Impurities such as arsenic, antimony, bismuth, selenium and tellurium may occur in the blister copper.

A dark colored, but perfectly adherent deposit is dissolved very slowly from the foil, in a covered electrolytic jar, by gently heating for several hours with about 60–70 cc. of a solution containing 2 cc. sulphuric and 5 cc. nitric acids. When the solution is complete the temperature is raised to expel dissolved gases. Five cc. saturated ammonium nitrate solution is added and the electrolyte diluted to 125 cc. When cooled to room temperature, electrolysis is carried out under the same conditions as that of the first deposit and on the same foil, if arsenic or antimony is the interfering impurity; on a fresh foil if selenium or tellurium has been the contaminating element. The undeposited copper is determined colorimetrically in the mixture of the first and final electrolytes and added to the weight of the copper deposited.

If the sample contains a large percentage of arsenic or antimony, a portion representing 2 grams is drawn from a pipette into a Kjeldahl flask, 10 cc. of sulphuric acid added, and the liquid boiled until nitric acid has been expelled. From this solution cuprous sulphocyanate is precipitated according to the method described on page 153. The funnel containing the filter is placed in a 500 cc. flask with long neck, the filter is punctured and the precipitate washed into the flask with the least quantity of water possible, the adherent precipitate is dissolved from the filter with warm dilute nitric acid, added cautiously to avoid violent evolution of gases from the dissolving precipitate in the flask. The washed filter is incinerated and the solution of its ash by nitric acid reserved for addition to the electrolyte after completion of electrolysis. When solution of the precipitate is complete, the liquid is boiled to small volume, neutralized, and 5 cc. ammonium nitrate solution and 3 cc. excess free nitric acid added. The liquid is transfered to an electrolytic jar and electrolysis carried out in the manner already described.

The amounts of bismuth, arsenic, antimony, selenium or tellurium usually found in blister copper may be precipitated together with iron present by addition of ammonia to a pipetted portion. The filtered precipitate is purified of copper by solution with nitric acid and reprecipitation. The combined filtrates are neutralized, 3½ cc. of free nitric acid added and the solution electrolyzed under the conditions already described. The nitric acid solution of the incinerated filter, carrying the iron, etc., is added to the electrolyte after electrolysis is complete. The undeposited copper is determined colorimetrically by one of the procedures outlined on pages 165, 166 or 167.

The deposited copper is never absolutely pure. The total impurities seldom exceed 0.03%. Ag from 0.000 to 0.18%; As from 0.000 to 0.003%; Sb from 0.000

to 0.004%; Se and Te from 0.001 to 0.027%; Bi from 0.000 to 0.0003%. Periodical complete analyses may be made and corrections applied to the analysis where exceedingly accurate percentages are required.

Too low a current density or excessive oxidizing power of the electrolyte may produce high results, due to the oxidation of the deposited copper. Too high a current density or a deficiency of oxidizing power in the electrolyte, by causing a deposition of impurities, will give high results.

The electrodes used by the Nichols Copper Co. are straight platinum wires for the positive anodes and cylinders 1¼ in. long, 1 in. in diameter of 0.004 in. iridoplatinum foil, 11½ sq. in. depositing surface, for the cathodes.

A uniform current is essential.

The nitric acid used should be free of iodic acid.

The presence of oxide of nitrogen gases, or a chloride in an acid solution, will cause a coarsely crystalline or brittle deposit, under conditions which in their absence would produce a good plating. The deposit moreover may contain platinum from the anode if the electrolyte contains a chloride salt.

Silver may be removed from the electrolyte by filtration, upon precipitation as a chloride, or it may be deposited with the copper and correction made for its presence from the result of a separate assay. In the latter case the copper deposits in poor form, unless the silver be first plated out at a very low current density.

Solid matter, unless removed, will contaminate the deposit mechanically.

Arsenic, antimony, selenium or tellurium have an influence on the physical character of the deposit which may affect the copper result beyond the sum of such impurities deposited.

In the process of preparing an electrolyte, arsenic may be eliminated as arsenious fluoride in the decomposition of selicious material by hydrofluoric acid. Selenium is expelled by evaporation to dryness of a hydrochloric acid solution or by fuming a sulphuric acid solution. All impurities may be removed by occlusion with ferric hydroxide, several times their weight of iron being added and the hydroxide then precipitated with ammonia. In the handling of copper solutions, account is to be taken of the retention of copper in the ferric hydroxide precipitate, and the combination of copper, in ammoniacal solution, with cellulose.

Whether impurities are deposited or not, appreciably high results are obtained by continuing electrolysis for some time after the electrolyte has become impoverished of copper. High results may also be obtained by a drop of current density below a desired limit whereby the copper is oxidized by the action of nitric acid. The same effect may also be brought about by too great an increase of temperature.

Overheating of the copper deposit, in the process of ignition of the alcohol clinging to the cathode, will cause oxidation of the copper. As much as possible of the alcohol must be shaken off before passing the electrode rapidly through the flame. It is advisable to weigh the copper shortly after deposition, as prolonged contact with air is undesirable, if extreme accuracy is desired.

The copper deposits may be removed by plunging the electrode, for a few moments, in hot nitric acid. After washing with water, the foil is ignited to a cherry red in a direct colorless flame. The ignition removes any grease which would be objectionable, that may contaminate the platinum. Alcohol frequently contains oily matter, which will cling to the electrode in spite of the rapid ignition for drying the deposit.

OTHER METHODS

Determination as Cuprous Sulphocyanate

The procedure has been outlined under Separations on page 153.

$$CuCNS \times 0.5226 = Cu.$$

Determination as Copper Oxide[1]

The solution, free from ammonium salts and organic matter, is heated to boiling in a porcelain dish and pure potassium hydroxide solution added, drop

[1] "Analytical Chemistry," Treadwell and Hall.

by drop, until a permanent precipitate, dark brown in color, is formed. The solution is alkaline to litmus-paper. The precipitate is washed by decantation, transferred to the filter and washed with hot water free of alkali. The precipitate and filter are ignited in a porcelain dish, first gently and finally with the full heat of a Bunsen burner. The residue is weighed as CuO.

$$CuO \times 0.7989 = Cu.$$

VOLUMETRIC METHODS FOR THE DETERMINATION OF COPPER

Potassium Iodide Method

The procedure depends upon the fact that cupric salts when heated with potassium iodide liberate iodine, the cuprous iodide formed being insoluble in dilute acetic acid is thus removed, no reversible reaction taking place.

Reactions. $2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$.

The liberated iodine is titrated with standard thiosulphate.

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$

This method is exceedingly accurate. Very few metals interfere. Bismuth, selenium, trivalent arsenic, antimony or iron should not be present. Lead, mercury, and silver increase the consumption of iodide, but do not otherwise interfere.

Solutions. ***Sodium Thiosulphate.*** 7.5 grams of the salt, $Na_2S_2O_3 \cdot 5H_2O$, are dissolved and made to 2 liters with water. The solution is standardized against a copper solution containing 1 gram of pure copper per liter, 1 cc. = 0.001 gram Cu. Approximately the same amount of copper is taken as will be determined in the ores. For high-grade copper ores and crude copper, etc., it is advisable to prepare a standard thiosulphate solution ten times the above strength. The copper solution is made slightly ammoniacal and then acid with acetic acid. Potassium or sodium iodide crystals, free from iodate, are added and the liberated iodine titrated with the standard thiosulphate. (See Procedure.)

$$\frac{\text{Weight of copper taken}}{\text{cc. thiosulphate required}} = \text{value of 1 cc. of the thiosulphate solution.}$$

Standard Copper Solution. One gram of purest electrolytic copper is dissolved in 20 cc. of dilute nitric acid, sp.gr. 1.2, and the solution diluted to 1000 cc. For standardizing the thiosulphate to be used with high-grade copper ores, crude copper, blister copper, etc., a copper solution containing ten times the above amount of metallic coppers is prepared.

The following additional reagents are required: starch solution, solid potassium iodide, 50% acetic acid solution, and other common laboratory reagents.

NOTE. Sodium thiosulphate is apt to change in strength upon standing, so that restandardization is necessary.

Procedure. The solution containing the copper, separated from interfering elements, by precipitation with aluminum powder or potassium sulphocyanate, is evaporated to about 30 cc. and the free acid neutralized with sodium carbonate, or ammonia, and then made slightly acid with acetic acid, 1 : 3, the solution becoming clear, about 3 grams of potassium iodide, or the equivalent

of a saturated solution, are added and the liberated iodine titrated with standard thiosulphate, the reagent being added until the brown color changes to light yellow and after the addition of starch solution until the blue color fades out. The end-point is very sharp.

Cc. thiosulphate multiplied by value of reagent gives weight of copper in sample.

NOTES. Nitrous oxides should be expelled before neutralizing with alkalies. A large excess of acetic acid should be avoided. The solution should be cool and contain at least 6 parts of KI for 1 of Cu, e.g., 1 Cu = 5.2231 KI = 1.9965 I = 3.9034 $Na_2S_2O_3 \cdot 5H_2O$. The solution should be concentrated, 40 to 50 cc.

Prof. Gooch recommends a volume of 100 cc., containing no more than 3 cc. nitric, sulphuric, or hydrochloric acids, or 25 cc. of 50% acetic acid, with 5 grams potassium iodide. Two to 3 grams more of potassium iodide are added if the titrations are large. "Methods in Chemical Analysis."

When ferric iron is the only disturbing impurity and no nitrates are present, the necessity of separation of copper may be avoided by fixing the free mineral acid by use of sodium acetate and then adding a clear, 4½ per cent solution of sodium fluoride until the red color of ferric acetate has bleached and then an excess of 10 cc. (Jour. Sci. Chem. Ind., May 15, 1915, p. 452; Mott, Chemist Analyst, July, 1912.)

Arsenic or antimony when present in trivalent form may be oxidized by treatment with bromine, chlorine, hydrogen peroxide or potassium permanganate, care being taken to expel or reduce any excess of the oxidizing agent before titration.

Potassium Cyanide Method

This procedure is largely employed on account of its simplicity, although it does not possess the degree of accuracy of the Iodide Method. The procedure depends upon the decoloration of an ammoniacal copper solution by potassium cyanide.

The operations of the standardization of potassium cyanide and of making the assay should be as near alike as possible. If iron is present in the assay it should be added to the standard copper solution titrated, in order to become accustomed to the end-point in its presence.

Silver, nickel, cobalt, cadmium, and zinc interfere and should be removed if present in appreciable quantities. Precipitation of metallic copper by aluminum powder, as directed under Separations, is recommended as a procedure for iron ores and briquettes. In presence of smaller amounts of iron, the titration may be made in presence of iron suspended in the solution. It is not advisable to filter off this precipitate, as it invariably occludes copper. With practice, the shade of color the iron precipitate assumes at the end of the reaction serves as an indicator, so that the operator is assisted rather than retarded by its presence.[1]

$$2Cu(NH_3)_4SO_4 \cdot H_2O + 7KCN = K_3NH_4Cu_2(CN)_6 + NH_4CNO + 2K_2SO_4 + 6NH_3 + H_2O.$$

Standard Potassium Cyanide Solution. Thirty-five grams of the salt are dissolved in water, then diluted to 1000 cc.

Standardization. 0.5 gram of pure copper is dissolved in a flask by warming with 10 cc. of dilute nitric acid (sp.gr. 1.2), the nitrous fumes expelled by boiling, solution neutralized, diluted and titrated as directed under Procedure.

[1] Sutton, "Volumetric Analysis." Davies, C. N., 58, 131. J. J. and C. Beringer, J., 49, 3. Dr. Steinbeck, Z. a. C., 8, 1; C. N., 19, 181.

If iron is present in the samples titrated, it is advisable to add iron to the standard copper solution as directed above.

$$\frac{0.5}{\text{cc. KCN solution}} = \text{wt. Cu per cc. of standard KCN.}$$

Procedure. The solution containing the copper is neutralized with sodium carbonate or hydroxide, the reagent being added until a slight precipitate forms. One cc. of ammonium hydroxide is now added and the solution titrated with standard potassium cyanide solution. The blue color changes to a pale pink; finally a colorless solution is obtained. In presence of iron, when the copper is in excess of the cyanide, the iron precipitate possesses a purplish-brown color, but, as this excess lessens, the color becomes lighter until it is finally an orange brown, the solution appearing nearly colorless. The reagent should be added from a burette drop by drop as the end-point is approached.

Cc. KCN × factor per cc. = weight Cu in assay.

COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER

Potassium Ethyl Xanthate Method

The method is based upon the fact that potassium ethyl xanthate produces a yellow-colored compound with copper. The reagent added to a solution containing traces of copper will produce a yellow color varying in intensity in direct proportion to the amount of copper present. Larger amounts of copper with the reagent produce a bright yellow precipitate of copper xanthate. Small quantities of iron, lead, nickel, cobalt, zinc, or manganese do not interfere. The procedure is especially valuable for determination of the purity of salts crystallized in copper pans.

Special Solutions. ***Stock Solution of Copper Sulphate.*** 3.9283 grams $CuSO_4 \cdot 5H_2O$ are dissolved in water and made up to a volume of 1000 cc. One cc. is equivalent to 0.001 gram Cu.

Standard Copper Sulphate. Ten cc. of the stock solution are diluted to 1000 cc. with distilled water. One cc. = 0.00001 gram Cu.

Potassium Ethyl Xanthate Solution. One gram of the salt is dissolved in 1000 cc. of water. The solution is kept in an amber-colored glass-stoppered bottle.

Procedure. Five grams of the substance are dissolved in 90 cc. of water (see note) and the solution poured into 100-cc. Nessler tube; 10 cc. of the potassium xanthate reagent are added and the solution mixed by means of a glass plunger. To a similar tube containing 50 or 60 cc. of water are added 10 cc. of the xanthate reagent and then gradually drop by drop the standard copper solution from a 10-cc. burette (graduated in $\frac{1}{10}$ cc.) until the colors in both tubes match.

If a = grams of the substance taken for analysis, b = number of cc. standard copper solution required to match the sample; then $b \times 0.00001 \times 100 \div a = \%$ Cu.

NOTES. The amount of the substance to be taken varies according to its copper content. The greater the copper contamination of the salt, the less sample required.

The solution should be neutral or only very slightly acid.

In place of the Nessler tubes the special colorimetric apparatus described under Titanium and under Lead may be used. A very weak copper standard will be required for the comparison tube.

If the substance is insoluble in water the copper is rendered soluble by treatment with nitric acid. Hydrochloric acid is added and the nitric expelled by evaporation. The substance is taken up with water and the insoluble residue filtered off.

Starch and organic matter are destroyed by addition of 10 cc. 10% sodium hydroxide+10 cc. of saturated sodium nitrate solution, then evaporating to dryness and igniting. Hydrochloric acid is now added to expel the nitric acid as directed above.

Ferrocyanide Method for Determination of Small Amounts of Copper

By this colorimetric method it is possible to detect one part of copper in 2,500,000 parts of water. The procedure depends upon the purplish to chocolate-brown color produced by potassium ferrocyanide and copper in dilute solutions. The procedure is applicable to the determination of copper in water and may be used in presence of a number of elements that occur in slags. Iron also produces a colored compound with ferrocyanide (1 part Fe detected in 13 million parts H_2O), so this element must be removed from the solution before testing for copper.

Solutions. ***Standard Copper Solution.*** 0.393 gram $CuSO_4 \cdot 5H_2O$ per liter. 1 cc. = 0.0001 gram Cu.

Ammonium Nitrate. 100 grams of the salt per liter.

Potassium Ferrocyanide. Four grams of the salt per 100 cc. of solution.

Procedure. A volume of 5 to 20 drops of potassium ferrocyanide, according to the amount of copper present in the solution, is placed in a tall, clear, glass cylinder or Nessler tube of 150 cc. capacity, 5 cc. of ammonium nitrate solution added and then the whole or an aliquot portion of the neutral [1] solution of the assay. The mixture is diluted to 150 cc. The same amount of ferrocyanide and ammonium nitrate solutions are poured into the comparison cylinder, placed side by side with the one containing the sample, on a white tile or sheet of white paper. The standard copper solution is now run from a burette into the comparison cylinder, stirring during the addition, until the color matches that of the assay. The number of cc. required multiplied by 0.0001 gives the weight of copper in the sample contained in the adjacent cylinder.

$$\frac{\text{Amount of Cu} \times 100}{\text{Wt. of sample compared}} = \% \text{ Cu in the sample.}$$

NOTES. The solution must be neutral, as the copper compound is soluble in ammonium hydroxide and is decomposed by the fixed alkalies. If the solution contains free alkalies, it is made slightly acid and then the acid neutralized with ammonia, added in slight excess. This is boiled to expel the excess of ammonia, and then tested according to the directions under "Procedure." Solutions containing free acids are neutralized with ammonia.

Iron may be removed by precipitation with ammonia. As this hydroxide occludes copper, the precipitate should be dissolved and reprecipitated to recover the occluded copper.

Determination of copper in water is accomplished by evaporating a quantity of water to dryness, taking up the residue with a little water containing 1 cc. nitric acid, the residue having been ignited to destroy organic matter, precipitating iron with ammonia, as directed above, and determining copper in the filtrate.

The colorimeter used in determination of traces of lead and for the colorimetric determination of titanium may be employed in place of the Nessler tubes.

Ammonia Method for Determining Small Amounts of Copper

In the absence of organic matter, nickel and elements giving a precipitate with ammonia, copper to an upper limit of 10 milligrams can be determined by comparison of the depth of the blue tint of its ammonium solution with a temporary or permanent standard copper solution of equal volume. Permanent standard solution of copper sulphate, free of nitrate, if kept cool and away from the direct sunlight, lasts for a long time.[1]

Hydrogen Sulphide Method

In the absence of elements precipitated by hydrogen sulphide, copper to the limit of about 1 milligram, in a solution not too strongly acid with sulphuric or hydrochloric acid, may be determined by comparison of its sulphide with that of a known quantity of copper in equal volume and similarly treated. The liquid should be cold and the passage of the hydrogen sulphide stopped before the compound coagulates.

NOTE. Either the ammonia or the hydrogen sulphide method is applicable to the determination of the copper not deposited in the operation of the electrolytic method.

DETERMINATION OF IMPURITIES IN BLISTER AND REFINED COPPER

Introduction. In the complete analysis of copper the following impurities are generally estimated: silver, gold, lead, bismuth, arsenic, antimony, selenium, tellurium, iron, zinc, cobalt, nickel, oxygen, sulphur, and less commonly, tin and phosphorus. In high grades of blister and in refined copper the percentage of these impurities is very low, the blister copper usually averaging over 99.0% copper with silver and the refined copper over 99.93% of the metal. The principal impurity in the refined element is oxygen, which may be present to the extent of .02 to .10%, the remaining impurities being in the third decimal place. From this it is readily seen that large samples are required for the accurate determination of these constituents. The amount of sample taken in blister copper depends upon the grade of copper analyzed. The impurities in this vary from tenths of a per cent to thousandths, as the meta' from one locality may contain quite appreciable amounts of a constituent, which may be present only in extremely small quantities or not at all in copper from a different section. In usual practice it is customary to take from 10 to 50 grams of blister and 50 to 500 grams of refined copper for analysis, depending upon the purity of the material. If a larger sample than 50 grams is taken, it is necessary to divide the material into several lots, and, after removal of the bulk of copper and isolation of the impurities, to combine the filtrates or residues containing the constituents sought.

In the procedures the smallest amount of sample, 10 grams, is taken as the basis of calculation for amounts of reagents used. For larger samples, in the initial treatment for removal of copper, proportionately larger amounts of the reagents are required, i.e., multiples of from 2 to 5 times the amount stated. A 50-gram sample is the largest amount of material handled in one lot.

Scrupulous care must be exercised throughout the analysis to prevent con-

[1] Heath, Jour. Am. Chem. Soc., 19, 21.

tamination of the sample or reagents, and to avoid loss of constituents. The reagents used should be free from the substance sought or from interfering substances. It is the practice to carry blank tests of the reagents through under conditions similar to a regular analysis for iron, lead, zinc, arsenic antimony and sulphur.

It is found best to determine the impurities in several portions, i.e., gold and silver by assay; bismuth and iron in one portion; lead, zinc, cobalt, and nickel in a second; arsenic, antimony, selenium, and tellurium in a third; and separate portions for sulphur, oxygen, phosphorus and tin, when these are occasionally required.

Determination of Bismuth and Iron

Separation of Copper. ***Amount of Sample.*** Blister copper 10 to 25 grams, refined copper 100 to 500 grams. The drillings are dissolved in a large beaker in 40 cc. of nitric acid per 10-gram sample and the free acid expelled by boiling. The solution should not become basic during the evaporation. Water is added to make the volume 130 cc. per 10 grams or proportionately more for larger samples. Ammonia is now added in sufficient excess to hold the copper in solution and 5 cc. of saturated ammonium carbonate solution and the sample diluted to 200 cc. (25 cc. $(NH_4)_2CO_3$ per 50 grams, and dilution to 1000 cc.). The beaker is placed on the steam bath for several hours, preferably over night. The solution is filtered hot (to avoid crystallization of the copper salt), the first 100 cc. being refiltered, and the residue washed with hot water containing a little ammonia. By this procedure the copper passes into the filtrate and bismuth and iron remain in the residue on the filter.

Separation of Iron and Bismuth. The precipitate is dissolved in warm, dilute hydrochloric acid (1 : 3), ammonia added to the solution in sufficient amount to almost neutralize the acid and the solution then saturated with hydrogen sulphide. After settling some time, the precipitate containing bismuth sulphide is filtered off, iron passing into the solution.

Determination of Iron. Hydrogen sulphide is expelled by boiling the filtrate, and iron oxidized by addition of hydrogen peroxide, or potassium chlorate (nitric acid should not be used). The solution is evaporated to dryness and iron then determined in the residue by the stannous chloride method, details of which may be found in the chapter on Iron, page 221.

Determination of Bismuth. The sulphides remaining on the filter are dissolved in nitric acid, the solution evaporated with sulphuric acid to SO_3 fumes to expel nitric acid, the concentrate diluted with water, and lead filtered off. Bismuth is precipitated in the filtrate by addition of ammonia in slight excess, followed by 10 cc. of a saturated solution of ammonium carbonate, and boiling. The precipitate is settled for several hours or over night if preferred, and then separated by filtration. This is now dissolved in the least amount of nitric acid, added to the filter drop by drop from a burette and bismuth determined in the solution by the cinchonine iodide method, given in detail in the chapter on Bismuth, page 69.

NOTES. An excess of nitric acid, or the presence of cadmium, lead, silver, or hydrochloric acid interferes with the colorimetric procedure.

In analysis of refined copper several 50-gram portions are taken for analysis, ten such portions on a 500-gram sample; the filtrates, obtained upon dissolving the residue freed from copper, are combined and bismuth and iron determined on this combined solution.

Determination of Lead, Zinc, Nickel, and Cobalt

Removal of Copper. Ten to 25 grams of blister copper, and 100 to 250 grams of refined copper in 25-gram portions are taken for analysis. The metal is dissolved in nitric acid (40 cc. per 10 grams) and the solution boiled until a faint green precipitate begins to appear on the surface of the solution. The free acid being expelled, the solution is made faintly acid by adding 1 to 2 cc. of nitric acid, the solution diluted 300 to 700 cc., according to the amount of copper taken, and then electrolyzed with a current of 1.5 to 2 amperes for thirty-six hours, with a spiral anode and a cathode with about 160 cm. depositing surface. The solution should remain slightly acid throughout the electrolysis, otherwise cobalt, nickel, and zinc may be precipitated as hydroxides from a neutral solution. When the copper is nearly removed, the electrodes are disconnected, and removed.

The solution is concentrated by boiling, a few crystals of oxalic acid added. and the anode (which may be coated with PbO_2) immersed in the hot solution for a few minutes, then rinsed off into the solution.

Separation of Lead. The solution is evaporated to small volume, about 40 cc. of dilute sulphuric acid (1 : 1) are added and the mixture evaporated to SO_3 fumes. The cooled concentrate is diluted with 100 cc. of water and again evaporated to fumes. About 300 cc. of water added and when the soluble salts have dissolved, the solution is filtered and the residue, $PbSO_4$, washed. The filtrate contains Zn, Ni, Co, etc.

Determination of Lead. The residue, $PbSO_4$, is dissolved by successive treatments with ammonium acetate and hot water, the lead precipitated from the solution, made slightly acid with acetic acid, by adding a slight excess of potassium chromate and the element determined as lead chromate according to the standard procedure for lead. See page 236 in the chapter on Lead.

Removal of the Hydrogen Sulphide Group. The filtrate from the lead sulphate is saturated with H_2S and filtered. The filtrate contains zinc, cobalt, and nickel. To recover any occluded zinc, the precipitate is dissolved in nitric acid, taken to fumes with sulphuric acid, diluted to about 200 cc., and again treated with H_2S. The filtrate from this precipitate is combined with the first portion. The precipitate is rejected.

Removal of Iron. This, if present, will be found in the filtrate. The H_2S is expelled by boiling and the solution concentrated to 400 cc. after adding 5 cc. of H_2O_2 to oxidize the iron. Five grams of ammonium sulphate are added, the solution made strongly ammoniacal, and filtered. Iron is precipitated as $Fe(OH)_3$ and is thus removed. If much iron is present, a double precipitation is advisable to recover any occluded zinc, nickel, or cobalt, and the filtrates combined.

Determination of Zinc. The filtrate from iron is concentrated to 400 cc., then made neutral to litmus by cautious addition of dilute sulphuric acid, drop by drop, and then faintly acid with 3 drops in excess. Zinc is now precipitated as the sulphide by saturating the solution with H_2S and allowing to stand over night. The sulphide is filtered off. The filtrate contains cobalt and nickel.

Zinc sulphide is dissolved in hot dilute HCl (1 : 2) and a few crystals of $KClO_3$. The solution is evaporated to dryness, the residue taken up water containing a few drops of HCl and the extract filtered. (To remove any SiO_2 dis-

solved from the beakers.) Zinc carbonate is now precipitated (in a beaker of glass, which does not contain zinc) from the filtrate by addition of sodium carbonate, and ignited to the oxide ZnO.

$$ZnO \times 0.8034 = Zn.$$

Determination of Nickel and Cobalt. The filtrate from the zinc sulphide is examined for nickel and cobalt. About 0.5 cc. of sulphuric acid is added. H_2S is expelled by boiling, and 2 cc. of H_2O_2 added. The solution is concentrated to about 400 cc. (this should be free from nitric acid), treated with about 25 cc. of ammonium hydroxide, and electrolyzed over night with a current of 0.5 amperes. Nickel and cobalt, if present, are deposited on the cathode as metals and so determined. For greater details, consult the chapter on Nickel under the method by electrolysis.

Determination of Arsenic, Antimony, Selenium, and Tellurium

Separation of Copper. Ten to 50 grams of blister copper and 100 to 500 grams of refined copper are required for the determination. (For 500-gram sample, 5 lots of 100 grams are taken.) The drillings are dissolved in nitric acid (40 cc. per 10 grams) and the solution boiled until a light-green precipitate appears on the surface. The liquor is diluted to 500 cc., and 5 cc. of ferric nitrate containing 3% of iron are added. A basic acetate precipitate is now made, weak sodium hydroxide being added to neutralize the free acid, but not in sufficient amount to produce a permanent precipitate. If the end-point is overrun, nitric acid is added drop by drop until the solution clears. The solution is diluted to about 800 cc., 20 cc. of a saturated solution of sodium acetate added, the liquor brought to boiling and filtered hot through a large creased filter paper, the first portion of the filtrate being poured back on the filter. The residue is washed twice with hot water to remove the copper. Five cc. additional iron are added to the filtrate and a second basic acetate precipitation made, a separate filter being used. The precipitates are dissolved in the least amount of nitric acid necessary and the solutions combined. The liquor is concentrated to 150 cc., a pinch of potassium chlorate added, and the concentration continued until the volume has been reduced to about 30 cc. An equal volume of strong hydrochloric acid is added and a second pinch of chlorate and the evaporation repeated to eliminate all traces of nitric acid.

The evaporation is best conducted in a casserole, resting in the circular opening of an asbestos board, in order that the sides of the vessel may be protected from the flame.

Separation and Determination of Arsenic. The solution is transferred to a distillation flask, arsenic reduced with ferrous chloride, and distilled according to the standard procedure for this element, p. 33.[1] In this distillate arsenic is determined volumetrically.[2] (See chapter on subject.) Antimony, selenium and tellurium remain in the flask.

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[1] concentration should not be carried below 30 cc.

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flask after the elimination of arsenic. The antimony is now distilled, strong hydrochloric acid being introduced in the distilling flask drop by drop by means of a separatory funnel, to replace the solution distilled, the volume in the flask being kept as low as possible, avoiding crystallization. When the antimony has been completely eliminated, the contents of the distilling flask is poured out while still hot, and, together with the rinsings of the flask, placed aside for the subsequent determination of selenium and tellurium.

The distillate is neutralized with ammonia, then made slightly acid with HCl and antimony precipitated with H_2S. Most of the selenium and tellurium remain in the flask. Some of the selenium, however, distills with the antimony, hence this must be recovered from the antimony sulphide precipitate and at the same time this must be purified.

The precipitate is dissolved in dilute HCl (1 : 2), containing a little bromine to oxidize the sulphur. The solution is filtered free from sulphur and the filter washed with a little dilute HCl. The filtrate should contain one-third its volume of strong HCl. Selenium is now precipitated by passing in SO_2 gas to saturation and bringing the solution to boiling. The precipitate is allowed to settle several hours and then filtered through a tared Gooch crucible. (To this is added the selenium and tellurium later obtained from the residue of the flask.) The filtrate contains antimony.

After boiling out the SO_2, the filtrate is first neutralized with ammonia, then made slightly acid with hydrochloric acid and antimony precipitated as the sulphide by saturating the solution with H_2S, allowing the precipitate to settle, resaturating with H_2S and again allowing to settle. The filtered, washed precipitate is dissolved with sodium sulphide, and 10 cc. of 25% potassium cyanide (poison) added to the filtrate, together with 2 cc. of 25% sodium hydroxide.

The solution is now electrolyzed hot (90° C.) for an hour with a current of 0.5 ampere and antimony deposited as the metal on the cathode. This is quickly removed and washed by dipping it successively into a beaker of cold water, three of hot water and one of 95% alcohol. The foil is dried at 100° C., and then weighed, on cooling, as usual. Antimony is now removed by immersing the cathode in boiling nitric acid containing tartaric acid, and washing as before. The loss of weight of the foil is taken as antimony.

NOTE. It is advisable to test the electrolyte for antimony by acidifying the solution with oxalic acid (Hood). A reddish coloration indicates the incomplete removal of the element.

Determination of Selenium and Tellurium. The solution from the distillation flask is nearly neutralized with ammonia and saturated with H_2S. The precipitate is filtered off and dissolved in equal parts of nitric acid (sp.gr. 1.42) potassium bromide bromine solution (20 cc. Br added to a saturated solution of KBr and diluted to 200 cc.). The liquor is diluted to 400 cc., 5 cc. of ferric nitrate (3% Fe''') solution added, and sufficient ammonia to make the solution decidedly alkaline. The precipitate contains, besides the iron, all of the selenium and tellurium, whereas any copper that may have been present is removed. The precipitate, washed, is dissolved in hydrochloric acid, the free acid nearly neutralized and H_2S passed in to saturation. The precipitate is filtered off, washed, and dissolved in the nitric acid potassium bromide and bromine mixture stated above. The solution is filtered and then sufficient hydrochloric acid added to make the solution contain about one-third its volume of strong HCl. Selenium and tellurium are precipitated from this solution by pass-

ing in SO_2 to saturation, and boiling for a minute or so. The precipitate is now filtered into the crucible containing the selenium obtained in the purification of the antimony precipitate. After washing with hot water and once with 95% alcohol, the residue is dried at 100° C. for an hour and weighed as selenium and tellurium.

NOTE. The precipitate of selenium and tellurium may contain gold, which should be determined by assay.

Determination of Oxygen

This determination is required only in refined copper. The method depends upon the reduction with hydrogen of cuprous oxide, heated to redness, the water formed by the reaction being the measure of the oxygen.

Apparatus. The combustion-furnace is the same as that used for the determination of carbon. As it is necessary that the hydrogen be absolutely free from oxygen and moisture, the gas is passed through a preheater, consisting of a platinum or silica tube of small bore heated to redness by a flame or an electrical device. The gas is then passed through a tube containing calcium chloride and finally through a P_2O_5 bulb containing the anhydride. In this purified form it enters the combustion-tube. The product of combustion, water, is absorbed in a tared bulb by P_2O_5, to which is attached a tube of calcium chloride.

Procedure. The sample, which has been drilled with considerable care to avoid overheating, is dried under partial vacuum in a desiccator after warming to below 70° C. for a few minutes.

One hundred grams are taken for analysis and placed in the combustion tube, the drillings being held in a large boat. Purified hydrogen is rapidly passed through the tube for half an hour to sweep out the air, the tube being cold. The tared P_2O_5 bulb and the calcium chloride tube are now attached. The heat is turned on to bring the sample to red heat (about 900°) and the current of hydrogen passed slowly over the sample for several hours.

The increase of weight of the P_2O_5 bulb $= H_2O$.

$$H_2O \times 0.8881 = O. \quad O \times 4.9687 = CuO.$$

Determination of Sulphur

This determination is rarely required in refined copper.

Twenty grams of blister, unrefined or cement copper, placed in a casserole, are treated cold with 50 cc. bromine-potassium bromide mixture (see under Determination of Selenium and Tellurium). After standing at least ten minutes, 100 cc. of strong nitric acid are added. After another ten minutes the casserole is placed on the steam bath and the solution evaporated to small volume. This is taken up with 25 cc. of strong hydrochloric acid and evaporated to a pasty mass. The treatment is repeated to ensure the decomposition of nitrates and to expel nitric acid. It is now taken up with 5 cc. of hydrochloric acid, diluted with water and sulphuric acid precipitated as $BaSO_4$, according the standard procedure for sulphur. See p. 395.

$$BaSO_4 \times 0.1374 = S.$$

Determination of Phosphorus

This determination is seldom required, and then only in low-grade copper and copper scrap containing phosphor bronze. The sample, dissolved in nitric acid, is treated with ferric nitrate and the basic acetate precipitation made as has been described for the determination of arsenic, etc. The precipitate is dissolved in HCl, this solution then made strongly ammoniacal, and saturated with H_2S, and filtered. The filtrate containing the arsenic and phosphoric acid is acidified, arsenic sulphide and sulphur filtered off, and phosphoric acid determined in the filtrate by precipitation with magnesia mixture as usual. See chapter on Phosphorus.

$$Mg_2P_2O_7 \times .2787 = P.$$

DETERMINATION OF COPPER IN REFINED COPPER

In determining the quality of copper for electrical purposes each hundredth of a percent above 99.90 has its significance. The methods employed are the electrolytic and the hydrogen reduction methods.

Electrolytic Method.[1] The sample, consisting of unground drillings, should be untarnished, free of grease or oil, and cleaned of particles of iron by use of a good magnet.

Procedure. A catch weight of about 5 grams is taken, each piece being examined for dust, particles from the drill and surface oxidation, before it is placed on the balance pan. Solution is effected in a special 400 cc. beaker, which has hipped sides to support a series of watch glasses, the lower hip at the 125 cc. mark, the upper at 350 cc. (Fig. 32.)

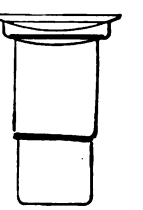

FIG. 32.

The drillings are treated with 50 cc. of a stock solution (10.5 p rts nitric acid and 4.5 parts of sulphuric). The watch-glass traps are put in place to retain the copper which is always entrained in the nitrogen peroxide fumes. Except that the current is maintained at .75 ampere throughout the period of electrolysis, the conditions are the same as have been described for the determination of copper by the "Small Portion Method." (Page 159.)

Hydrogen Reduction Method. This method is applicable to the determination of copper in such grades of refined copper, which are cha acterized by a metallic impurity content which is constant and is less than 0.01 percent. The apparatus consists of a combustion furnace, preferably electrolytically heated, the temperature of which can be kept constant at about 950° C.; a silica tube of ¾ in. bore, one end of which is connected with a large Peligot tube containing concentrated sulphuric acid, the other end is connected by a rubbe· plug and flexible tube with a source of purified hydrogen; porcelain combustion boats 95 mm. long, 18 mm. wide and 10 mm. deep.

Procedure. A catch weight of about 25.1 grams of drillings is placed in the combustion boat, and the boat inserted in the silica tube. After passing hydrogen for half an hour through the cold tube, the temperature is raised to 950° C. and so maintained for two hours. If the furnace is of a type, which will permit the removal of the tube without disconnecting the train,[2] the tube is taken from the

[1] Ferguson, Jour. Ind. and Eng. Chem., May, 1910.
[2] Electric Heating Apparatus Co., New York.

solved from the beakers.) Zinc carbonate is now precipitated (in a beaker of glass, which does not contain zinc) from the filtrate by addition of sodium carbonate, and ignited to the oxide ZnO.

$$ZnO \times 0.8034 = Zn.$$

Determination of Nickel and Cobalt. The filtrate from the zinc sulphide is examined for nickel and cobalt. About 0.5 cc. of sulphuric acid is added. H_2S is expelled by boiling, and 2 cc. of H_2O_2 added. The solution is concentrated to about 400 cc. (this should be free from nitric acid), treated with about 25 cc. of ammonium hydroxide, and electrolyzed over night with a current of 0.5 amperes. Nickel and cobalt, if present, are deposited on the cathode as metals and so determined. For greater details, consult the chapter on Nickel under the method by electrolysis.

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flask after the elimination of arsenic. The antimony is now distilled, strong hydrochloric acid being introduced in the distilling flask drop by drop by means of a separatory funnel, to replace the solution distilled, the volume in the flask being kept as low as possible, avoiding crystallization. When the antimony has been completely eliminated, the contents of the distilling flask is poured out while still hot, and, together with the rinsings of the flask, placed aside for the subsequent determination of selenium and tellurium.

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The precipitate is dissolved in dilute HCl (1 : 2), containing a little bromine to oxidize the sulphur. The solution is filtered free from sulphur and the filter washed with a little dilute HCl. The filtrate should contain one-third its volume of strong HCl. Selenium is now precipitated by passing in SO_2 gas to saturation and bringing the solution to boiling. The precipitate is allowed to settle several hours and then filtered through a tared Gooch crucible. (To this is added the selenium and tellurium later obtained from the residue of the flask.) The filtrate contains antimony.

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NOTE. It is advisable to test the electrolyte for antimony by acidifying the solution with oxalic acid (Hood). A reddish coloration indicates the incomplete removal of the element.

Determination of Selenium and Tellurium. The solution from the distillation flask is nearly neutralized with ammonia and saturated with H_2S. The precipitate is filtered off and dissolved in equal parts of nitric acid (sp.gr. 1.42) potassium bromide bromine solution (20 cc. Br added to a saturated solution of KBr and diluted to 200 cc.). The liquor is diluted to 400 cc., 5 cc. of ferric nitrate (3% Fe''') solution added, and sufficient ammonia to make the solution decidedly alkaline. The precipitate contains, besides the iron, all of the selenium and tellurium, whereas any copper that may have been present is removed. The precipitate, washed, is dissolved in hydrochloric acid, the free acid nearly neutralized and H_2S passed in to saturation. The precipitate is filtered off, washed, and dissolved in the nitric acid potassium bromide and bromine mixture stated above. The solution is filtered and then sufficient hydrochloric acid added to make the solution contain about one-third its volume of strong HCl. Selenium and tellurium are precipitated from this solution by pass-

FLUORINE

WILFRED W. SCOTT

F', *at.wt.* 19; D (*air*) 1.31$^{15°}$, *sp.gr.* (−187°) 1.14; *m.p.* −223; *b.p.* −187° C; *acids*, HF, H_2SiF_6.

DETECTION

Fluorine is the most active element known, and is by far the most active of the halogens, displacing chlorine, bromine, and iodine from their combinations.

Etching Test. The procedure depends upon the corrosive action of hydrofluoric acid on glass, the acid being liberated from fluorides by means of hot concentrated sulphuric acid. This test is applicable to fluorides that are decomposed by sulphuric acid. The reactions taking place may be represented as follows:

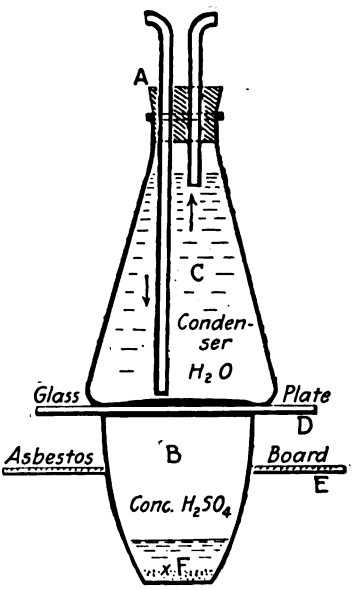


FIG. 33.—Etching Test for Fluorine.

I. $CaF_2+H_2SO_4=CaSO_4+2HF$.

II. $SiO_2+4HF=2H_2O+SiF_4$.

The test may be carried out in the apparatus shown in the illustration, Fig. 33. A clear, polished glass plate 2 ins. square, free from scratches, is warmed and molten wax allowed to flow over one side of the plate, the excess of wax being drained off. A small mark is made through the wax, exposing the surface of the plate, care being exercised not to scratch the glass. If the test is to be quantitative, the marks should be of uniform length and width. The powdered material is placed in a large platinum crucible (*B*) (a lead crucible will do); sufficient concentrated sulphuric acid is added to cover the sample. The plate (*D*) with the wax side down is placed over the crucible and pressed firmly down. To prevent the wax from melting, a condenser (*C*), with flowing water, cools the plate. An Erlenmeyer flask (*C*) is an effective and simple form of condenser, though a metallic cylinder is a better conductor of heat. A little water placed on the plate makes better contact with the condenser. As a further protection a wide collar of asbestos board (*E*) may be placed as shown in the figure. In quantitative work, where a careful regulation of heat is necessary, the crucible is placed in a casserole with concentrated sulphuric acid or in a sand bath, containing a thermometer to register the temperature. The run is best conducted at a temperature of 200° C. (not over 210°—H_2SO_4 fumes).

After an hour the wax is removed with hot water and the plate wiped clean, and examined by reflected light for etching. A test is positive when the mark can be seen from both sides of the glass. Breathing over the etched surface intensifies the mark.

Treatment of Fluo-Silicates not Attacked by Sulphuric Acid. The powdered material is mixed with about eight times its weight of sodium carbonate and fused in a platinum crucible. The cooled melt is extracted with water. Calcium fluoride is thrown out from the filtrate, according to directions under Preparation and Solution of the Sample. The fluoride may now be tested as directed in the etching test or as follows by the hanging drop test.

The Hanging Drop Test. The test depends upon the reaction $3SiF_4+3H_2O=2H_2SiF_6+H_2SiO_3$.

If the material contains carbonates, it is calcined to expel carbon dioxide. Half a gram of the powdered dry material is mixed with 0.1 gram dried precipitated silica and placed in a test-tube, Fig. 34, about 5 cm. long by 1 cm. in diameter. A one-hole rubber stopper fits in the tube. A short glass tube, closed at the upper end, passes through the stopper extending about 3 mm. below. Two or three drops of water are placed in this small tube by means of a pipette, nearly filling it. Two cc. of concentrated sulphuric acid are added to the sample in the test-tube and this immediately closed by inserting the stopper carrying the hanging drop tube, exercising care to avoid dislodging the drop of water. The test-tube is placed in a beaker of boiling water and kept there for thirty minutes. If an appreciable quantity of fluorine is present a heavy gelatinous ring of silicic acid will be found at the end of the hanging drop tube in the stopper.

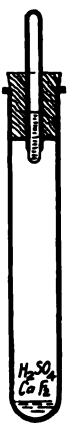


FIG. 34.
Hanging Drop Test for Fluorine.

It is important to have material, test-tube, and rubber stopper dry, so that the deposition may occur as stated.[1]

NOTE. Dr. Olsen[2] makes the test by heating the sample in a small Erlenmeyer flask, with concentrated sulphuric acid. A watch-crystal with a drop of water suspended on its curved surface is placed over the mouth of the flask. A spot etch is obtained in presence of fluorine.

Black Filter Paper Test. According to Browning,[3] small amounts of fluorine may be detected by the converse method for detection of silicates and fluosilicates (See silicon). The fluoride is placed with a suitable amount of silica, in a small lead cup, 1 cm. in diameter and depth (Fig. 35); a few drops of concentrated sulphuric are added; the cup is covered by a flat piece of lead with a small hole in the center; upon the cover is placed a piece of moistened black filter paper and upon this a small pad of moistened filter paper. The cup is heated on the steam bath for ten or fifteen minutes. A white deposit will

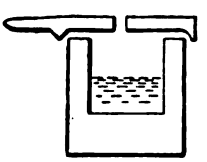


FIG. 35.

[1] C. D. Howard; Jour. Am. Chem. Soc., 1906, **28**, 1238–1239. C. N., 1906, **30**, 420.

[2] Communicated to the author by J. C. Olsen.

[3] P. E. Browning, Am. Jour. Sci. (4), **32**, 249. "Methods in Chemical Analysis," by F. A. Gooch.

be found on the under side of the black filter paper, over the opening in the cover, if fluorine is present in an appreciable amount. (0.001 gram CaF_2 or above, and 0.005 gram Na_3AlF_6 will give the test.)

ESTIMATION

The determination of fluorine in the evaluation of minerals used for the production of hydrofluoric acid is of technical importance. The demand for elimination of the use of fluorides for preservatives of food makes its estimation in small amounts of importance.

Fluorine occurs only combined. It is found abundantly combined with lime in the mineral fluorspar, CaF_2. It occurs as cryolite, Na_3AlF_6; apatite, $3Ca_3(PO_4)_2CaF_2$. It is found in mineral springs, ashes of plants, in bones, and in the teeth (CaF_2). It occurs sparingly, with aluminum and silicon, in topaz, and with cerium and yttrium in fluocerite, yttrocerite, also in wavellite, wagnerite, etc.

Preparation and Solution of the Sample

Fluorides of the alkalies, and of silver and mercury, are readily soluble; copper, lead, zinc, and iron fluorides are sparingly soluble; the alkaline earth fluorides dissolve in 100 cc. H_2O as follows: $BaF_2 = 0.163$ gram, $SrF_2 = 0.012$ gram, $CaF_2 = 0.0016$ gram.

Fluosilicates of potassium, sodium, and barium are slightly soluble in water and practically insoluble if sufficient alcohol is added.

Organic Substances.[1] These are best decomposed by the lime method, the details of which are given in the chapter on chlorine under the section for the preparation and solution of the sample, p. 122. For fluorides in organic matter it is advisable to decompose the substance in a seamless nickel tube, 40 mm. long by 4–5 mm. bore. The end of the tube is sealed with silver solder. The lime used should be soluble in acetic acid. The tube is heated to yellow heat for two hours. The lime is then extracted with acetic acid and fluorine determined as calcium fluoride.

Silicious Ores and Slags. 0.5 to 1.0 gram of material is fused in a crucible with ten times its weight of sodium and potassium carbonates (1 : 1) and poured into an iron mould. If a porcelain crucible has been used, this is broken up and added to the cooled fusion. The mass is digested with about 200 cc. of hot water for an hour, the mass having been broken up into small lumps, (Kneeland recommends using an agate-ware casserole as diminishing the liability of subsequent bumping)[2] then boiled briskly for ten minutes longer and filtered, the solution being caught in a large beaker. The residue is washed with hot water, followed by a hot solution of ammonium carbonate and the insoluble material rejected. The silica is removed with ammonium carbonate, followed by the zinc oxide treatment of the second filtrate, as described under the section of Separations. In presence of appreciable amounts of fluorides, the gravimetric precipitation of fluorine as calcium fluoride is recommended.

[1] H. Meyer and A. Hub, Monatsch. für Chem., 1910, **31**, 933–938. C. N., 1910, **35**, 489.

[2] E. Kneeland, Eng. and Min. Jour., 80, 1212. A. H. Low, "Technical Methods of Ore Analysis."

Calcium Fluoride. The product is best decomposed by fusion with sodium and potassium carbonates, after mixing the fluoride with two and one-half times as much silicic acid (Treadwell and Hall) the greater part of the silicic acid and all the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate. The mixture must be heated gradually to prevent the contents of the crucible from running over the sides by a rapid evolution of carbon dioxide. The thin liquid fusion soon changes to a thick paste. The reaction is complete when there is no further evolution of carbon dioxide. The fused mass is now extracted with hot water as indicated above, and the soluble fluoride filtered from the calcium carbonate residue. Silicic acid is removed from the filtrate by addition of ammonium carbonate. Traces of silicic acid are removed from the filtrate taken to near dryness, after neutralizing the alkali with dilute hydrochloric acid (phenolphthalein indicator), by the zinc oxide emulsion method given under Separations. Fluorine is precipitated as calcium fluoride, according to the procedure given later on page 180.

Soluble Fluorides. The salts are dissolved in water. In presence of free acid a platinum dish should be used and the acid neutralized with sodium carbonate with addition of about one-fourth as much more in excess. The fluoride is then precipitated as calcium fluoride.

Hydrofluoric Acid. The acid may be titrated with standard caustic. Determined gravimetrically, the acid is neutralized and fluorine precipitated as calcium fluoride or lead chlorofluoride (pages 180, 181).

Valuation of Fluorspar. Details of the procedure worked out by E. Bidtel, Chief Chemist, Fairview Fluorspar and Lead Company, are given at the close of the chapter.

SEPARATIONS

Removal of Silicic Acid from Fluorides. This separation is frequently required, especially in samples where the sodium and potassium carbonate fusion has been required for decomposition of fluosilicates, or calcium fluoride mixed with silicic acid. (See section on Preparation and Solution of the Sample.)

To the alkaline solution about 5 to 10 grams of ammonium carbonate are added, the solution boiled for five minutes and allowed to stand in the cold for two or three hours. (Treadwell and Hall recommend heating to 40° C., and allowing to stand over night.) The precipitate is filtered off and washed with ammonium carbonate solution. The fluoride passes into the filtrate, while practically all of the silicic acid remains on the filter.

Small amounts of silica in the filtrate are removed by evaporating the solution to near dryness on the water bath, then neutralizing the carbonate with dilute hydrochloric acid (phenolphthalein indicator) added to the residue taken up with a little water. Upon boiling the pink color is restored, the solution then cooled and acid again added to discharge the color; this is repeated until finally the addition of 1–2 cc. of 2 N. HCl is sufficient to discharge the color. Four to 5 cc. of ammoniacal zinc oxide solution (moist ZnO dissolved in NH_4OH—Low recommends 20 cc. of an emulsion of ZnO in NH_4OH) is added and the mixture boiled until ammonia has been completely expelled. The precipitate of zinc silicate and oxide is filtered and washed with water. The fluoride is determined in the filtrate by precipitation with calcium chloride as directed later.

Separation of Hydrofluoric and Phosphoric Acids. The method of Rose modified by Treadwell and Koch,[1] takes advantage of the fact that silver phosphate is insoluble in water, whereas silver fluoride is soluble. The alkaline solution of the two acids (aqueous solution of the sodium carbonate fusions) is carefully neutralized with nitric acid and transferred to a 250-cc. calibrated flask. A slight excess of silver nitrate solution is added, and the mixture made to volume and thoroughly shaken. After settling, the solution is filtered through a dry filter, the first 10 cc. being rejected. Two hundred cc. of this filtrate is again transferred to a 250-cc. calibrated flask, the excess of silver precipitated by adding sodium chloride solution, and after diluting to the mark and shaking, the precipitate is again allowed to settle; 200 cc. of this solution is taken for analysis, after filtering as previously directed. This sample represents 64% of the original sample taken. Fluorine is now determined by one of the procedures outlined.

Separation of Hydrofluoric and Hydrochloric Acids. The solution containing hydrofluoric and hydrochloric acids, in a platinum dish, is treated with nitric acid and silver nitrate. The chloride is precipitated as the silver salt, whereas the fluorine remains in solution and may be filtered off through a glass funnel coated with paraffine or wax, or a hard rubber funnel. In presence of phosphoric acid, silver nitrate added to the solution will precipitate the phosphate as well as the chloride, whereas the fluoride remains in solution. The phosphate may be dissolved out from the chloride by means of dilute nitric acid.

Separation of Hydrofluoric and Boric Acids. An excess of calcium chloride is added to the boiling alkali salt solutions of the two acids. The precipitate is filtered off and washed with hot water. The residue, consisting of calcium fluoride, borate and carbonate, is gently ignited and then treated with dilute acetic acid, taken to dryness, and the residue taken up with acetic acid and water. Calcium acetate and borate are dissolved, whereas the fluoride remains insoluble and may be filtered off and determined.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

Precipitation as Calcium Fluoride

The method utilizes the insolubility of calcium fluoride in dilute acetic acid in its separation from calcium carbonate, the presence of which facilitates filtration of the slimy fluoride. The reaction for precipitation is as follows:

$$2NaF + CaCl_2 = CaF_2 + 2NaCl.$$

Procedure. Solution of the sample and the removal of silica having been accomplished according to procedures given under Preparation and Solution of the Sample, and Separations, the solution is neutralized, if acid, by the addition of sodium carbonate in slight excess; if basic, by addition of hydrochloric acid in excess, followed by sodium carbonate. To this solution, faintly basic, 1 cc. of twice normal sodium carbonate reagent is added, followed by sufficient

[1] Z. anal. Chem., **43**, 469, 1904. "Analytical Chemistry," Vol. 2, by Treadwell and Hall.

calcium chloride solution to precipitate completely the fluoride and the excess of carbonate, i.e., until no more precipitate forms, and then 2–3 cc. in excess. After the precipitate has settled, it is filtered and washed with hot water. (The filtrate should be tested for fluoride and carbonate with additional calcium chloride.) The precipitate of calcium fluoride and carbonate is dried and transferred to a platinum dish, the ash of the filter, burned separately, is added and the material ignited. After cooling, an excess of dilute acetic acid is added, and the mixture evaporated to dryness on the water bath. The lime is converted to calcium acetate, while the fluoride remains unaffected. The residue is taken up with a little water, filtered and washed with small portions of hot water, by which procedure calcium acetate is removed, while calcium fluoride remains on the filter.[1] The residue is dried, separated from the filter and ignited. This, together with the ash of the filter, is weighed as calcium fluoride, CaF_2.

To confirm the result, the residue is treated with a slight excess of sulphuric acid and taken to fumes in a platinum dish. The adhering acid is removed as usual by heating with ammonium carbonate, and the ignited residue weighed as calcium sulphate. One gram of calcium fluoride should yield 1.7436 grams of calcium sulphate.[2]

$$CaO \times 1.3924 = CaF_2, \text{ or } \times 0.677 = F.$$

Factors. $CaF_2 \times 0.4867 = F$, or $\times 0.5126 = HF$, or $\times 1.0757 = NaF$. $CaSO_4 \times 0.5735 = CaF_2$, or $\times 0.2937 = F$, or $\times 0.2539 = HF$.

Precipitation of Fluorine as Lead Chlorofluoride

The method, worked out by Starck,[3] takes advantage of the double halide formed by action of lead chloride upon a soluble fluoride. The compound, PbFCl, is about fourteen times the weight of the fluorine it contains. Unfortunately, the compound is quite appreciably soluble in water,[4] so that a loss occurs if pure water is used for washing the precipitate. The method is limited to the determination of soluble fluorides.

The sample, made neutral, is treated with a large excess of a cold saturated solution (200 cc. $PbCl_2$ per 0.1 gram NaF in 50 cc. solution) of lead chloride, the precipitate, settled over night, is filtered off in a weighed Gooch crucible, washed several times with a saturated solution of lead chlorofluoride, and finally two or three times with ice-cold water. The compound is dried two hours at 140–150° C., and weighed as PbFCl.

[1] The results are slightly low, owing to the solubility of calcium fluoride: 100 cc. H_2O dissolves 0.0016 gram CaF_2; 100 cc. 1.5 N. $HC_2H_3O_2$ dissolves 0.011 gram.

[2] Low recommends disintegration of the fluoride with sulphuric acid, diluting the mixture with water, boiling with ammonium chloride, and then with ammonium hydroxide and hydrogen peroxide. Calcium oxalate is now precipitated from the filtrate and CaO determined by titration with standard permanganate according to the usual procedure for determination of lime.

[3] Z. anorg. Chem., **70**, 173 (1911); Chem. Abs., **5**, 2049 (1911).

[4] One hundred grams H_2O at 18° C. dissolves 0.0325 gram PbFCl and 0.1081 gram at 100° C.

VOLUMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

Volumetric Determination of Fluorine—Formation of Silicon Tetrafluoride and Absorption of the Evolved Gas in Water. Offerman's Method [1]

Silicon tetrafluoride is formed by the action of sulphuric acid upon a fluoride in presence of silica, the evolved gas is received in water and the resulting compound titrated with standard potassium hydroxide. The following reactions take place:

$$A.\quad 3SiF_4+2H_2O=2H_2SiF_6+SiO_2.$$

$$B.\quad H_2SiF_6+6KOH=6KF+SiO_2+4H_2O.$$

The method is suitable for determining fluorine in fluorspar in evaluation of this mineral.

Procedure. The powdered sample, containing the equivalent of 0.1–0.2 gram calcium fluoride, is mixed with about three times its weight of pulverized quartz (previously ignited and kept in a desiccator), placed in the decomposition flask *F*, shown in Fig. 36, and about 1 gram of anhydrous copper sulphate

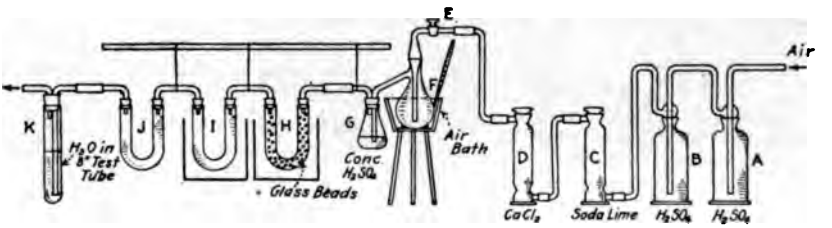


FIG. 36.

added, followed by 25 cc. of concentrated sulphuric acid. The stopcock *E* is closed and the air bath heated gradually till in one-half hour the temperature has risen to 220°. The cock *E* is now opened and air slowly forced through the apparatus (by means of water pump) at the rate of about three bubbles per second, the temperature being kept at 220°, and the flask containing the sample occasionally shaken. When the bubbles of silicon tetrafluoride have disappeared from *F*, the flame is removed, but the air current continued for half an hour longer. The solution in the receiving flask is now titrated with 0.1 N. KOH.

NOTES. The apparatus shown in the cut is the form recommended by Adolph, and the details of procedure are essentially his. This method is preferred to that of Penfield,[2] in which an alcoholic solution of potassium chloride is used to absorb the tetrafluoride, and the liberated hydrochloric acid titrated with the standard alkali in presence of cochineal indicator.

The results obtained by this method are generally low, but the procedure is useful for rapid valuation of fluorspar.

[1] Z. angew. Chem., **3**, 615 (1890). Wm. H. Adolph, Jour. Am. Chem. Soc., **37**, 11, 2500 (1915).

[2] Am. Chem. Jour., **1**, 27 (1879).

The bottles *A*, *B*, *C*, and *D* are for the purpose of thoroughly drying the air, as moisture in the apparatus is to be avoided. *G* contains strong sulphuric acid, *H* is filled with glass beads to remove sulphuric acid spray, *I* and *J* are empty tubes, which should be thoroughly dry. The gas is completely absorbed in *K*.

Volumetric Determination of Fluorine—Ferric Chloride Method [1]

The procedure, worked out by Greef, depends upon the principle that a neutral aqueous solution of ferric chloride forms a white crystalline precipitate with neutral solutions of alkali fluorides, the following reaction taking place:

$$6NaF+FeCl_3=Na_3(FeF_6)+3NaCl.$$

The double fluoride is only very slightly soluble in water and does not form the red compound $Fe(CNS)_3$ with sulphocyanates. The addition of sodium chloride makes the precipitation more complete.

Procedure. Half a gram sample of the sodium or potassium salt is placed in a 300-cc. Erlenmeyer flask, and dissolved in about 25 cc. of hot water, then cooled and 20 grams of sodium chloride and 5 cc. of potassium sulphocyanate added (100 grams KCNS per 500 cc. H_2O). The solution is titrated with a standard solution of ferric chloride (of such strength that 100 cc. is equivalent to about 1 gram of NaF) until a yellow color is produced. Ten cc. of alcohol and 10 cc. of ether are now added and the mixture shaken gently, then the flask closed and shaken vigorously. The titration is now continued until the ether layer is permanently colored red.

NOTE. Commercial sodium fluoride frequently contains free hydrofluoric acid and silico-fluoride. These are converted to the fluoride of sodium by titration with sodium hydroxide in presence of phenolphthalein to neutral reaction; the total fluoride may now be determined as described.

The free acid may be determined by titrating the salt in an aqueous alcoholic solution in presence of potassium chloride, which converts the silico-fluoride to the insoluble potassium silico-fluoride.

Colorimetric Determination of Fluorine—Method of Steiger [2] and Merwin [3]

The method is based on the bleaching action of fluorine upon the yellow color produced by oxidizing a solution of titanium with hydrogen peroxide. A known amount of titanium in solution is mixed with definite volume of the solution containing the fluorine and the tint compared with a standard solution containing an equivalent amount of titanium. The extent of bleaching enables the computation of the fluorine present. The method is applicable to determination of fluorine in amounts ranging from 0.00005 to 0.01 gram. Merwin has shown that large amounts of alkali sulphates have a bleaching action similar to fluorine. Addition of free acid, or rise of temperature, intensifies the color lost by bleaching. Aluminum sulphate has no marked effect on standard solutions, or on solutions bleached by alkali sulphates, but it restores the color to a considerable degree to solutions bleached by fluorine. Ferric sulphate has a similar effect. Phosphoric acid bleaches a standard solution. Silica has little

[1] Method by A. Greef, Ber., **46**, 2511–2513 (1913). C. N., **7**, 3939 (1913). Jour. Soc. Chem. Ind., **32**, 992 (1913). Analyst, 1913, p. 521.

[2] G. Steiger, Jour. Am. Chem. Soc., **30**, 219, 1908.

[3] H. E. Merwin, Am. Jour. Sci. (4), **28**, 119, 1909. Chem. Abs., **3**, 2919 (1909).

effect. According to Merwin an accuracy of 0.002 gram may be expected, an error which is half that of the most reliable gravimetric method.

Reagents. ***Standard Titanium Solution.*** An intimate mixture of 1 gram of TiO_2 and 3 grams of ammonium persulphate is heated until the vigorous action has ceased, and the ammonium sulphate is expelled. The residue is treated with 20 cc. of strong sulphuric acid, heated to fuming and, when cold, poured into about 800 cc. of cold water. When the suspended salt has dissolved, 57.5 cc. of strong sulphuric acid are added, and the solution made up to 1000 cc. (50 cc. or more of the solution should be analyzed for TiO_2). *One cc. will contain* 0.001 *gram* TiO_2.

Standard Fluorine Solution. 2.21 grams of sodium fluoride, which has been purified by recrystallizing, washing, and igniting strongly, is dissolved in 1000 cc. of water. One cc. will contain 0.001 gram fluorine.

Sulphuric Acid. 95.5% solution, sp.gr., 1.84.

Hydrogen Peroxide. Ordinary strength.

Standard Colored Solution. The solution used in determining fluorine in materials fused with alkali carbonates contains 10 cc. of the titanium solution, 4 cc. of hydrogen peroxide, and 4 cc. of concentrated sulphuric acid.

Apparatus. ***Nessler Tubes*** 6 cm. long, 2.7 cc. in diameter are recommended by the authors. Colorimeters may be used in place of Nessler tubes. A very suitable type for this purpose is shown on page 245, Fig. 43.

Procedure. Two grams of the powdered sample are fused with 8 grams of mixed sodium and potassium carbonates, the fusion taken up with hot water, and when leached, 3 to 4 grams of ammonium carbonate added. The mix is warmed for a few minutes and then heated on the water bath till the ammonium carbonate is decomposed and the bulk of liquid is small. Silica, ferric oxide, and alumina oxide are thrown down and are removed by filtration. The filtrate, which should not exceed 75 cc., is treated with 4 cc. of hydrogen peroxide, and then 10 cc. of standard titanium solution cautiously added (H_2O_2 prevents precipitation of TiO_2 by the alkali carbonates), followed by 4 cc. of strong sulphuric acid to neutralize the alkali carbonates. The solution, neutral or slightly acid, acquires a light orange tint. A little sodium carbonate is added in just sufficient amount to discharge the color, and then a drop or so of acid to again restore it. The amount of excess acid now required depends upon the amount of fluorine present in the solution. For amounts of fluorine less than 0.0025 gram (0.125% of sample), 3 cc. of acid are added. For amounts of 0.025 to 0.012 gram fluorine, 12 cc. of acid are added. The solution is diluted to 100 cc.

Comparison. The test solution is now compared with the standard solution containing 10 cc. titanium reagent, and the same amount of acid and hydrogen peroxide as in the test sample, in a volume of 100 cc. If Nessler tubes are used, these are held over a white surface illuminated with diffused light. In the absence of a bleaching substance, such as fluorine, the two solutions will have the same tint, but in presence of fluorine the bleaching effect will cause the test solution to appear paler than the standard. The depths of the liquids are adjusted so that the tubes will have the same intensity of color when moved from right to left or reversed. Should the left eye perceive a darker shade, the tube on the left will appear uniformly darker whether it be the test sample or the standard. The comparative depths of the liquids in the tubes are measured and the ratio obtained by dividing the depth of the fluorine solution by the depth of the standard and multiplying by 100. Reference may be made to the

plotted curve shown in Fig. 37. The ratio $\frac{\text{Depth of F Sol.}}{\text{Depth of Standard}} \times 100 = \text{the}$

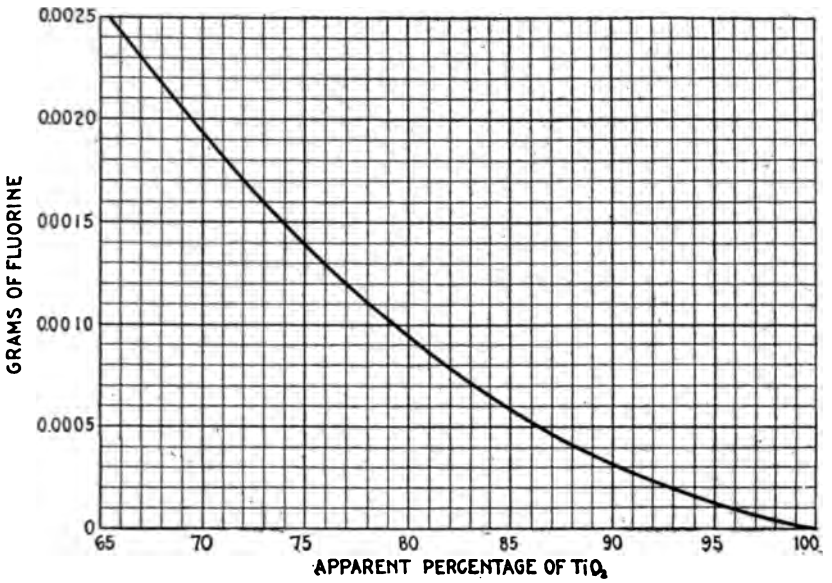


FIG. 37.

abscissa, while the ordinate represents the amount of fluorine in the 2-gram sample.

Example. Suppose the test solution = 3.6 cm. and the standard = 4.5 cm.,

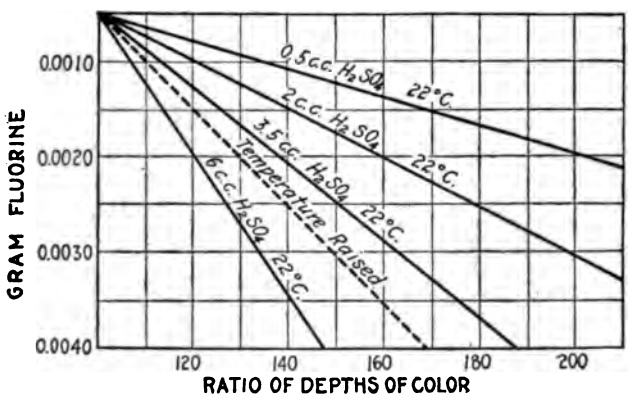


FIG. 38.

the ratio then = 80, from the curve it is evident that the fluorine = 0.00095 gram or 0.0475%, since a 2-gram sample was taken.

According to Merwin, however, the bleaching effect of alkali sulphates, which are present, will make the ratio much higher than it would be if they were absent. (The sulphates alone give a ratio of 125.) This ratio should be determined on two 8-gram portions of the alkali carbonate mixture used in the fusion and the correction made accordingly. If m = ratio of the blank thus obtained, and r the ratio of the final test, then the formula, according to Merwin, is $\frac{r-m}{23{,}000}$ = gram fluorine in the sample, 4 cc. excess sulphuric acid being used in the samples, or $\frac{r-m-3}{6300}$ = grams F, if 12 cc. of acid are used in testing larger amounts of fluorine. The plotted curve, Fig. 38, is that given by Merwin, and shows the effect of acidity on the depth of color obtained. The abscissa represents the ratio of the solutions, and the ordinate the amount of fluorine in grams. Temperature of the tests was 22° C.

VALUATION OF FELDSPAR

The following procedure, worked out by Dr. Bidtel,[1] meets the commercial requirements for the valuation of feldspar. The determinations usually required are calcium fluoride, silica, and calcium carbonate; in some particular cases lead, iron, zinc, and sulphur.

Procedure. Calcium Carbonate. One gram of the finely powdered sample is placed in a small Erlenmeyer flask, 10 cc. of 10% acetic acid are added, a short-stemmed funnel inserted in the neck of the flask as a splash trap, and the mixture heated for an hour on a water bath, agitating from time to time. The calcium carbonate is decomposed and may be dissolved out as the soluble acetate, whereas the fluoride and silica are practically unaffected. The solution is filtered through a 7-cm. ashless filter, the residue washed with warm water four times, and the filter burned off in a weighed platinum crucible at as low a temperature as possible. The loss of weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is reported as *calcium carbonate*.

Silica. The residue in the platinum crucible is mixed with about 1 gram of yellow mercuric oxide, in form of emulsion in water (to oxidize any sulphide that may be present); any hard lumps that may have formed are broken up, the mixture evaporated to dryness and heated to dull redness, then cooled and weighed. About 2 cc. of hydrofluoric acid are added and the mixture evaporated to dryness. This is repeated twice to ensure complete expulsion of silica (as SiF_4). A few drops of hydrofluoric acid are then added, together with some macerated filter paper, and a few drops of ammonium hydroxide to precipitate the iron. The solution is evaporated to dryness, heated to dull redness, cooled and weighed. The loss of weight is reported as *silica*.

Calcium Fluoride. The residue is treated with 2 cc. of hydrofluoric acid and 10 drops of nitric acid (to decompose the oxides), the crucible covered and placed on a moderately warm water bath for thirty minutes, the lid then removed and the sample taken to dryness. The evaporation with hydrofluoric acid is repeated to ensure the transposition of the nitrates to fluorides, and if

[1] Dr. E. Bidtel, Chemist, Fairview Fluorspar and Lead Company, Jour. Ind. Chem., Vol. 4, No. 3, March, 1912.

the residue is still colored, hydrofluoric acid again added and the mixture taken to dryness a third time; then a few drops of hydrofluoric acid are added and 10 cc. of ammonium acetate solution (the acetate solution is made by neutralizing 400 cc. of 80% acetic acid with strong ammonia, adding 20 grams of citric acid and making the mixture up to 1000 cc. with strong ammonium hydroxide). The mixture is digested for thirty minutes on a boiling water bath, then filtered and washed with hot water containing a small amount of ammonium acetate, and finally with pure hot water. (Several washings by decantation are advisable.) The residue is ignited in the same crucible and weighed as *calcium fluoride*. An addition of 0.0022 gram should be made to compensate for loss of CaF_2.

Pure calcium fluoride is white. To test the purity of the residue, 2 cc. of sulphuric acid are added and the material taken to fumes to decompose the fluoride; 1 cc. of additional sulphuric acid is added and the excess of acid expelled by heating. The residue is weighed as calcium sulphate. This is now fused with sodium carbonate, and the fusion treated with hydrochloric acid in excess. If barium is present the solution will be cloudy($=BaSO_4$.)

ANALYSIS OF SODIUM FLUORIDE

Preparation of the Sample and Insoluble Residue. Ten grams of the sample are dissolved in 250 cc. of water in a beaker, and boiled for five minutes, then filtered into a liter flask through an ashless filter; the residue is washed with several portions of water and ignited. This is weighed as insoluble residue. The filtrate and washings are made to 1000 cc. with distilled water.

Sodium Fluoride. Fifty cc. of the solution equivalent to 0.5 gram of sample are diluted to 200 cc. in a beaker, 0.5 gram sodium carbonate is added and the mixture boiled. An excess of calcium chloride solution is now added slowly and boiled for about five minutes. A small amount of paper pulp is added to prevent the precipitate from running through the filter, the precipitate allowed to settle and then filtered, using a 9-cm. S. & S. 590, or B. & A. grade A, filter paper. The fluoride is washed twice by decantation, and four or five times on the filter with small portions of hot water. The final washings should be practically free of chlorine.

The residue is ignited in a platinum dish, then treated with 25 cc. of acetic acid, and taken to dryness. This treatment is repeated and the residue taken up with a little hot water and filtered. The calcium fluoride is washed free of calcium acetate with small portions of water, remembering that CaF_2 is slightly soluble in water. The ignited residue is weighed as CaF_2.

$$CaF_2 \times 1.0757 = NaF.$$

Sodium Sulphate. To the filtrate from calcium fluoride is added 10 cc. hydrochloric acid and then a hot solution of barium chloride. The $BaSO_4$ is allowed to settle, filtered, washed, dried, ignited, and weighed as usual:

$$BaSO_4 \times 0.6086 = Na_2SO_4.$$

Sodium Carbonate. Sodium carbonate is determined on a 5-gram sample by the usual method for carbon dioxide as described in the chapter on Carbon.

Approximate results may be obtained by adding a small excess of normal sulphuric acid to 5 grams of the fluoride in a platinum dish, boiling off the carbon

dioxide, and titrating the excess of acid with normal caustic, using phenolphthalein indicator.

One cc. N. $H_2SO_4 = 0.053$ gram Na_2CO_3.

$H_2SO_4 \times 1.0816 = Na_2CO_3$.

Sodium Chloride. Fifty cc. of the sample is titrated with N/10 $AgNO_3$ solution.

Silica. This is probably present as sodium fluoride and silicate. One gram of the sample is dissolved in the least amount of water and a small excess of hydrofluoric acid added to convert the silicate to silico-fluoride, then an equal volume of alcohol. After allowing to stand for an hour, the precipitate is filtered, washed with 50% alcohol until free of acid and the filter and filtrate are placed in a beaker with 100 cc. of water, boiled and titrated with N/10 NaOH.

One cc. N/10NaOH = 0.0015 gram SiO_2 or 0.0047 gram Na_2SiF_6.

Volatile Matter and Moisture. One-gram sample is heated to dull redness to constant weight. Loss of weight is due to moisture and volatile products.

DETERMINATION OF TRACES OF FLUORINE

An approximate estimation of traces of fluorine may be made by utilizing the method outlined for detection of this element. The apparatus [1] is the same, with the exception that the crucible rests in a paraffine [2] bath containing a thermometer to regulate the temperature. A casserole may be used to hold the paraffine. By varying the amounts of substance tested an etch is obtained that is comparable with one of a set of standard etches, obtained with known amounts of fluorine in form of calcium fluoride, added to the same class of material examined.

The conditions in obtaining the standard etches and those of the tests should be the same. This applies to the temperature of the paraffine bath, duration of the run, size of mark exposing the surface of the test-plate, and the general mode of procedure.

NOTE. The importance of regulating the temperature may be seen by the results obtained by Woodman and Talbot. With a temperature of 79–82° C., one part of fluorine may be detected in 25 to 100 thousand parts of material; by raising the temperature to 136° C., the delicacy of the procedure is increased to one part of fluorine in 1 to 5 million parts. The limit of delicacy is apparently reached at 213–218° C. (i.e., 1 part F per 25 million).

[1] A metal condenser, such as is recommended for mercury determinations, may be used and the paraffine bath substituted by an electric heater automatically controlled.

[2] Crisco is claimed to be better than paraffine, as this does not give off any unpleasant fumes when heated.

GLUCINUM (BERYLLIUM)

W. W. Scott.

Gl, *at.wt.* 9.1; *sp.gr.* $1.85^{20°}$; *m.p.* > 960° C.; *oxide,* GlO.

DETECTION

In the usual course of analysis glucinum will be precipitated by ammonia along with iron and aluminum hydroxides. Silica having been removed by evaporation to dryness of the acid solution of the substance, extraction of the residue with dilute hydrochloric acid and subsequent filtration; the members of the hydrogen sulphide group are precipitated from slightly acid solution by hydrogen sulphide. The filtrate is concentrated to about 30 cc., and about 2 grams of sodium peroxide are added to the cooled liquid, which is now heated to boiling and filtered. $Fe(OH)_3$ remains insoluble, if iron is present, while aluminum and glucinum dissolve. The filtrate is acidified with nitric acid, and ammonia then added in excess. If a precipitate forms, alumina or glucinum or both are indicated. Glucinum hydroxide and aluminum hydroxide cannot be distinguished by appearance; the solubility of the former in sodium bicarbonate solution makes it possible to separate the two. The precipitate is dissolved in acid and the solution made almost neutral with ammonia. Solid sodium bicarbonate is added in sufficient amount to make the solution contain 10% of the reagent and the mixture heated to boiling, then filtered. Alumina hydroxide remains on the filter paper and glucinum passes into the filtrate, in which it may be detected by diluting to ten volumes with water and boiling, whereupon glucinum hydroxide precipitates.

Glucinum hydroxide, $Gl(OH)_2$, is precipitated from neutral or acid solution by ammonia, insoluble in excess (distinction from $Al(OH)_3$). It is precipitated by sodium and potassium hydroxides, soluble in excess (separation from iron); if this solution is boiled $Gl(OH)_2$ is reprecipitated, $Al(OH)_3$ remains in solution. $Gl(OH)_2$ is soluble in an excess of ammonium carbonate, $Al(OH)_3$ is insoluble.

ESTIMATION

Glucinum occurs in the minerals beryl, euclase, davalite, chrysoberyl, helvite, leucophane, phencaite.

The oxide, GlO, is soluble in strong sulphuric acid. It is decomposed by fusion with potassium fluoride. The freshly precipitated hydroxide, $Gl(OH)_2$, is easily soluble in dilute acids, in alkalies and alkali carbonates and bicarbonates.

The methods of preparation and solution of the sample are the same as those described for the estimation of aluminum. For details of these procedures the analyst is referred to the chapter on this element.

SEPARATIONS

Removal of Silica and Members of the Hydrogen Sulphide Group. See procedure given under "Detection."

Separation of Glucinum from Iron and Manganese. The acid solution is nearly neutralized with ammonia and then poured with constant stirring into an excess of a cold mixture of ammonium sulphide and carbonate. Iron and manganese are precipitated, whereas glucinum passes into the filtrate. (Zirconium and yttrium will be found with glucinum, if they are present in the material examined.)

Separation from Zirconium and Yttrium. The filtrate obtained from the separation of iron and manganese is boiled for an hour, the precipitate is filtered and washed, then dissolved in dilute hydrochloric acid. To this solution is added an excess of sodium hydroxide, zirconium and yttrium are precipitated, whereas glucinum remains in solution. After filtering, glucinum may be precipitated by boiling the diluted filtrate.

Separation from Aluminum, Chromium and Iron. The elements precipitated as hydroxides are ignited to oxides and fused with sodium carbonate for an hour or more. Upon leaching with water, aluminum and chromium dissolve, while iron and glucinum remain insoluble. The oxides of glucinum and iron may be separated by fusion with sodium acid sulphate, extracting with water and precipitating the iron with an excess of sodium hydroxide, glucinum remaining in solution.

Separation of Glucinum from Aluminum. The hydroxides of alumina and glucinum are precipitated with ammonia and the precipitate treated with an excess of ammonium carbonate. $Gl(OH)_2$ dissolves, whereas $Al(OH)_3$ remains insoluble. See Detection, also Gravimetric Method for Determination of Glucinum.

GRAVIMETRIC DETERMINATION OF GLUCINUM

The procedure recommended by Parsons and Barnes [1] depends upon the solubility of glucinum hydroxide in a 10% sodium bicarbonate solution, in the separation of this element from iron and aluminum hydroxide precipitate, with which it is commonly thrown out from solution. (Uranium, if present, also dissolves.)

Procedure. Silica and the members of the hydrogen sulphide group having been removed by the usual methods (See Detection), hydrogen sulphide is expelled by boiling, nitric acid is added in sufficient amount to oxidize iron (the hydrochloric acid solution turns yellow) and ammonium hydroxide added in slight excess. The precipitated hydroxides are allowed to coagulate by heating to boiling and, after settling a few minutes, filtered and washed with a 2% solution of ammonium acetate containing free ammonia.

Separation from Iron and Aluminum Hydroxide. The precipitate is dissolved in hydrochloric acid, the solution oxidized with nitric acid or hydrogen peroxide (C.P.), if necessary, and the free acid then neutralized with ammonia. To the cold solution are added 10 grams of sodium bicarbonate for each 100 cc.

[1] C. L. Parsons and S. K. Barnes, Jour. Am. Chem. Soc., **28**, 1589, 1906.

of liquid. The mixture is heated to boiling and boiled for one minute,[1] then cooled and filtered. The residue is washed with hot 10% solution of sodium bicarbonate. Iron and aluminum hydroxides remain on the filter and glucinum passes into the filtrate.

To recover occluded glucinum from the hydroxides of iron and alumina, the precipitate is dissolved in a few drops of hydrochloric acid, and the precipitation repeated. It is advisable to repeat this treatment a third time, adding the filtrates to the first portion containing the glucinum.

Precipitation of Glucinum. The combined filtrates from the alumina and iron hydroxides are acidified with strong hydrochloric acid, the beakers covered to prevent loss by spurting and the carbon dioxide completely removed by boiling. (CO_2 remaining in solution would form ammonium carbonate, on subsequent treatment with ammonia, which would dissolve glucinum.) A slight excess of ammonia is now added, the mixture again boiled and the precipitated glucinum hydroxide allowed to settle, then filtered and washed with a 2% solution of ammonium acetate containing free ammonia, until the chlorides are removed. After ignition the residue is weighed as glucinum oxide, GlO.

$$GlO \times 0.3626 = Gl.$$

[1] Prolonged boiling would cause the loss of too much CO_2, so that $Al(OH)_3$ would be apt to pass into solution. The evolution of CO_2 may be mistaken for boiling.

GOLD

W. G. DERBY

Au, *at.wt.* 197.2; *sp.gr.* 19.33; *m.p.* 1063; *b.p.* 2530° C; *oxides*, Au_2O, Au_2O_3

DETECTION

Because of the limited application and tediousness of wet methods, the detection of a small quantity (2 parts per million or less) of gold in a mineral or base metal is most positively carried out by furnace methods of assaying. Wet methods of detection of traces of gold can be applied only to solutions free of colored salts and elements precipitated by the reagents employed. As a rule, in the treatment of an unknown substance, advantage is taken of the solubility of most metals and their compounds, and insolubility of gold by one of the mineral acids.

Detection of Gold in Alloys. In metals or alloys which produce colorless solutions with dilute nitric acid, gold, in the absence of other insoluble matter, exhibits itself as a black or brownish residue which settles readily, and from which the liquid can be separated by careful decantation. If unassociated with metals of the platinum group, this residue will become yellowish brown on heating with strong nitric acid.

In copper, nickel and such alloys, which leave a residue of sulphur, carbon or silicious matter on treatment with dilute nitric acid, the solution is filtered through double ashless filters and the filter and residue incinerated in a porcelain crucible. The residue, which may require pulverizing, is digested for a few minutes with aqua regia, and the dilute, filtered solution evaporated to dryness by heating below 200° F. Just as soon as dry, the mass is moistened with the least quantity of hydrochloric acid and the purple of Cassius test applied to its water solution in a small volume. This test is made by adding a solution of stannous chloride, containing stannic chloride. In strongly acid and concentrated gold solutions a precipitate of brown metallic gold is obtained. If the solution is but slightly acid and dilute, a reddish purple color is produced by colloidal gold and the stannic acid. The tint fades on standing. Addition of ammonia produces a red coloration.

This test applied to 1 part of gold in 600,000 of solution will impart a perceptible shade; to double this quantity, a mauve color. When gold is present in somewhat greater proportion a flocculent precipitate will form.

Test for Gold in Minerals. From minerals, in which the metal exists in unalloyed, or uncombined state, gold may be extracted by iodine in potassium iodide solution, or by chlorine or bromine water. All minerals containing sulphides should be roasted. In natural or roasted state the sample should be very finely pulverized, and usually yields the gold best if first digested with nitric acid and washed free of soluble salts. The sample in a flask is covered with bromine water, the flask closed with a plug and shaken frequently during a period of three

four hours. The purple of Cassius test is applied to the extract, removed by decantation after concentration.

If it is evident that base metals are present in the bromine water extract in quantity sufficient to mask the purple of Cassius test, hydrogen peroxide is added to the concentrated liquid, slightly alkaline with sodium or potassium hydroxide or carbonate.[1] After boiling the solution until hydrogen peroxide is removed, precipitated hydroxides or carbonates are dissolved by hydrochloric acid. Gold in exceedingly small quantity exhibits itself as a light-brown residue on a fine filter. This indication should be confirmed by a purple of Cassius test on the aqua regia solution of the residue; the test carried out in the same manner as on the residue from a solution of a metal.

Benzidine Acetate Tests. Maletesta and Nola[2] make use of benzidine acetate (1 gram benzidine dissolved in 10 cc. acetic acid and 50 cc. water) as a reagent in the detection of gold and platinum in quite dilute solutions. Gold gives a blue coloration which gradually changes to violet. The coloration is green in the presence of free acetic acid, changing to blue with addition of benzidine in excess. Platinum gives a blue flocculent precipitate, the formation of which is promoted by heating. Free mineral acids have no influence on the gold and retard the platinum reaction only in the cold. Since ferric salts give a blue coloration, stable only in excess of benzidine, their absence must be assured before application of the test for the precious metals. The limit of sensitiveness of the test is 35 parts for gold and 125 parts for platinum per 10,000,000.

Phenylhydrazine Acetate Test. E. Pozzi Escot[3] adds phenylhydrazine acetate to a very dilute gold solution which contains an excess of an organic acid (formic or citric). A violet coloration, permanent for several hours, is imparted. The depth of color is proportional to the quantity when the gold is present in less amount than one part in 500,000.

ESTIMATION

Solubility

Gold in massive form is practically insoluble in pure nitric, sulphuric or hydrochloric acids, but in the presence of oxidizing agents, is attacked appreciably by sulphuric, and actively by hydrochloric acid. Gold is found in minute quantity in the nitric acid[4] solution of its alloys and in such as contain selenium, the amount may be a large part of the total present.

Gold is attacked energetically by aqua regia. Large amounts of gold are dissolved with requirement of least attention when the proportion of hydrochloric acid is several times that of the aqua regia formula, ($3HCl : 1HNO_3$).

Gold is dissolved by solutions of chlorine or bromine, by alkaline thiosulphates; in the presence of free oxygen by iodine in potassium iodide solution, by soluble cyanides, by fused potassium or sodium hydroxide; by fused potassium or sodium nitrate or sulphide. In a finely divided state, it is dissolved by a solution of potassium or sodium hydroxide.

Gold alloys quickly with molten lead. When in the form of bright, untarnished particles it alloys readily with mercury.

[1] Vanino and Seeman, Berichte, **32**, 1968; Rossler, Zeit. Anal. Chem., **49**, 733.
[2] Bull. Chim. Farm, **52**, 461; Chem. Abs., April 20, 1397, 1914.
[3] Am. Chim. Anal. Appl., 1907, **12**, 90; J.S.C.I., June 15, 1907, 645.
[4] Dewey, J.A.C.S., March, 1910, 318; E. Keller, Bull. Am. Inst. Min. Eng., **67**, 681.

GRAVIMETRIC METHODS

Gold is always weighed in metallic state, and is determined most accurately in the form of the mass obtained by dilute nitric acid treatment of the silver alloy resulting from the operation of cupellation in the method of assaying by furnace processes. On account of tediousness in making complete separation from associated metals, and of uncertainty in collection of the product in a form suitable for accurate weighing, direct precipitation methods are never used for the valuation of gold-bearing material, but may be applied to the estimation of gold in plating baths, the Wohlwill parting electrolyte and solutions of similar type.

Precipitation of Gold. From such solutions of auric chloride, slightly acid with hydrochloric, freed of oxidizing agents by evaporation and displacement with hydrochloric acid, and containing but little of the salts of the alkalis or alkali earths, gold is separated from other than occluded platinum and palladium by precipitation with oxalic acid, ferrous sulphate, or hydrazine hydrochloride. The reactions are hastened by heat. When salts of the alkalis or earths are present, equally good separation and more complete precipitation can be obtained by addition of excess of sodium peroxide, boiling vigorously for a few minutes and then acidifying with hydrochloric acid. The precipitated metal is collected on an ashless filter paper, and after drying, weighed.

Gold precipitated from a very weak solution is in such fine form that it is not wholly retained by the finest paper.

Wet Gold Assay of Minerals

A wet gold assay, suitable for prospector's use,[1] is carried out by covering one assay ton (29.17 grams), of the finely pulverized natural or roasted ore, in a porcelain mortar, with 50 cc. of a solution of 2 parts of iodine and 4 parts potassium iodide in 100 cc. of water. Sulphide ores should be roasted and digested with nitric acid before treatment with the iodine solution. Similar treatment is advantageously applied to all ores. The ore is ground in contact with the iodine solution and additions of the halogen are made whenever the liquid becomes colorless. The solution is then allowed to stand at least an hour. To the filtrate and washings from the pulp, in a glass-stoppered bottle or flask, are added 5 grams of gold free mercury. The liquid is shaken vigorously with the mercury until clear. The mercury is then transferred to a small porcelain casserole, washed with clean water and dissolved by warming carefully with 10 cc. nitric acid. The gold mass is washed free of nitrate of mercury by decantation, dried and annealed by heating in a casserole over a Bunsen flame, and the metal weighed. Each milligram represents an ounce per ton. Results obtained by this method of assaying are usually more than 50 per cent of the actual gold content.

Electrolytic Method. The gold content of a cyanide plating bath containing no potassium ferrocyanide may be estimated by electrolysis.[2]

Procedure. A measured quantity, 25 to 50 cc. in a tared platinum dish, is diluted to 1 cm. of the rim of the dish and using a carbon or platinum anode, elec-

[1] De Luce, Min. Sci. Press, **100**, 895; Hawson, Min. Sci. Press, **100**, 936; Davis, Mines and Minerals, Oct., 1910, Feb., 1911; Austen, Inst. of Min. and Met., May 31, 1911.

[2] Electro Deposition of Metals, Langbein.

trolyzed for about three hours at a current density $ND_{100} = 0.067$ amp. (.0.0043 per square inch). Completion of deposition is recognized by the lack of any deposit within fifteen minutes, on a platinum strip suspended on the rim of the dish. The dish plus gold deposit is washed, rinsed with alcohol, dried at 212° and when cold weighed.

The following is a summary of the conditions of deposition of gold in compact form as described by Classen [1] 3 grams potassium cyanide were added to a gold chloride solution containing 0.0545 grams of gold in 120 cc. This solution heated to about 55° C. when electrolyzed at a current density of $ND_{100} = 0.38$ amp. (0.024 amp. per square inch) with a potential difference of 2.7–4.0 volts, deposited its gold content in one and a half hours. Time required for deposition is tripled if the electrolyte is at room temperature.

Miller [2] deposited 0.1236 gram of gold in two and a quarter hours from 125 cc. of electrolyte at 50° C. containing 1 gram potassium cyanide by a current of $ND_{100} = 0.03$ amp. (0.002 amp. per square inch) and 2.5 volts.

Perkin and Preble [3] use an electrolyte containing ammonium thiocyanate in place of potassium or sodium cyanide.

Gold is removed from the platinum electrode by warming with a solution of chromic anhydride in a saturated salt solution,[4] or with a solution of potassium cyanide containing some oxidizing agent as hydrogen peroxide, sodium peroxide or alkali persulphate.[5]

VOLUMETRIC METHODS

These methods are applicable to the determination of the strength of chloride of gold solutions used in photography, electro gilding, and as electrolyte in the Wohlwill parting process.

Preparation of the Sample. Nitric acid or nitrates in the solutions should be removed by repeated evaporations to syrup with addition of hydrochloric acid saturated with chlorine. Free chlorine or bromine should be removed by addition of ammonia to formation of permanent precipitate, then making the solution very slightly acid with hydrochloric acid and heating until the precipitate of fulminating gold dissolves. The gold solution should contain but little free hydrochloric acid, an excessive amount of which may be removed by ammonia.

Permanganate Method

Weak gold solutions should be concentrated whenever possible. The permanganate method,[6] which is not applicable when the sample contains organic matter, depends upon the titration, after complete precipitation of gold, of the unoxidized portion of a measured quantity of an added reagent of a known gold precipitating value. The reagent may be ammonium or potassium oxalate, ferrous sulphate or ferrous ammonium sulphate in solutions varying from 5 to 25 milligrams gold precipitating value and is titrated with a permanganate solution of approximately equal oxidizing strength. One part of gold requires for precipitation 1.08 of ammonium oxalate, 1.40 of potassium oxalate, 4.22 of ferrous sulphate, 5.96

[1] Classen, "Quantitative Chemical Analysis by Electricity," Classen-Boltwood.
[2] J.A.C.S., Oct., 1904, 1255.
[3] Elec. Chem. and Met. Ind., 3, 490.
[4] Classen-Boltwood, "Quantitative Chemical Analysis by Electricity."
[5] Rose, "Met. of Gold," 5th Ed., 469.
[6] Bull. Chim. Farmac., 1894, XXX, III, 25; Oestr. Zeit. f. Berg. und Hut., 182, 1880; Sutton, "Volumetric Analysis," 10th Ed.; E. A. Smith, "Sampling and Assaying of Precious Metals"; Min. Eng. World, 37, 853.

parts ferrous ammonium sulphate, each in crystalline form. The most satisfactory precipitations are made with the iron salts. The standard solution of either should contain about 0.1 per cent of sulphuric acid. One part of gold, in solution as auric chloride, has an oxidizing value equivalent to 0.4808 part of potassium permanganate.

The precipitating value of 0.2548 gram of dry Sorenson's sodium oxalate is 250 milligrams of gold, and by titrating a solution of this amount of oxalate in 250 cc. of water, acidulated with a few drops of sulphuric acid, the oxidizing value of the permanganate solution is obtained in terms of gold.

The value of the precipitating reagent and relative oxidizing value of the permanganate solution can be checked very accurately by adding a measured quantity of the reagent to an excess of gold chloride, filtering, washing thoroughly, incinerating and weighing the precipitate obtained in a tared porcelain crucible.

Procedure. In carrying out the determination of a gold solution, a measured or weighed portion is freed of oxidizing agents, a measured amount of the standard precipitating reagent added in slight excess of the amount required to decolorize the solution, and digestion on a steam bath or hot plate continued until the gold settles out, leaving a clear liquid. A few drops of sulphuric acid may be then added and, without filtering, titration performed. The gold value of the quantity of reagent added, minus that found of the excess of reagent, is the gold content of the amount of the sample taken.

Iodide Method

Small quantities of gold are determined by Gooch and Morley's iodide method.[1] A measured or weighed portion of the gold solution is treated, as has been described for removal of oxidizing agents, with an excess of free hydrochloric acid. Potassium iodide solution is run into the cold liquid until the gold precipitated as aurous iodide is completely dissolved. Starch solution is then added, and the amount of N/1000 thiosulphate required to decolorize the liquid noted. From this amount is deducted the amount of N/1000 iodine required to just produce a perceptible rose tint in the liquid.

The reactions involved are $AuCl_3+3KI=AuI+I_2+3KCl$ and $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$.

The gold value of the N/1000 solution of sodium thiosulphate should be determined by performance of the operations of the method on a known quantity of gold, similar in amount and contained in a volume of solution approximately equal to that of the analysis.

Lenher's Method. By Lenher's method[2] of determining gold in solutions free of oxidizing agents, sulphurous acid of a reducing strength of 2–5 milligrams gold per cc. is used as the reagent. The sulphurous acid requires frequent standardizing by means of standard iodine or potassium iodide to which a definite amount of standard permanganate has been added or by a gold solution of known strength. Using starch as indicator, the iodine liberated by addition of potassium iodide can be titrated by sulphurous acid. Bromine liberated by potassium bromide according to the equation, $AuCl_3+2KBr=AuCl+2KCl+Br_2$, can be titrated by sulphurous acid. Excess of magnesium or sodium chloride gives to auric chloride a yellow color which by sulphurous acid can be titrated to the colorless or aurous state. These alkaline salts do not interfere in the potassium bromide or iodide reactions.

[1] Amer. Jour. Sci., Oct., 1899, 261; Min. and Eng. World, **37**, 853; Vol. Am., Sutton, 10th Ed.; "Assaying of Precious Metal," E. A. Smith.

[2] Jour. Am. Chem. Soc., June, 1913, 735.

COLORIMETRIC METHODS

Practical application of these methods is made in the estimation of gold in the liquors produced in the treatment of ores by the cyanide process.

Prister's Method

By Prister's method [1] a slight excess of copper solution is added to a 100 to 200-cc. portion of a cyanide solution in which the cyanide has been decomposed by boiling several minutes after acidifying with hydrochloric acid. Assurance of the presence of an excess of copper is made by spot test with a solution of potassium ferrocyanide.

The copper solution is made by boiling for ten minutes in contact with copper shavings, a solution of 1 part blue vitriol and 2 parts salt in 10 parts of water, and adding a little acetic acid on cooling. A few drops of a 1 to 2 % sodium sulphide solution are added, the liquid boiled for five minutes, the precipitate allowed to settle, and liquid separated by decantation on to a filter. The precipitate in the beaker and on the filter is dissolved with 2½ to 3 cc. of a 3 to 5% solution of potassium cyanide to which a few drops of potassium hydrate solution has been added.

Gold is precipitated from this cyanide solution (which may be turbid), by addition of 1 to 2 g ams of zinc dust and warming to 100° F. for half an hour. Liquid is separated by decantation through a filter. The residue on the filter and in the beaker is first treated with hydrochloric acid to dissolve zinc, then with 10 cc. aqua regia, the reagent being passed several times through the filter. Stannous chloride solution is then added to the liquid diluted to 20 cc. Comparison of the coloration produced is made with that from a standard solution of gold treated in the same manner.

Cassel's Method. By Cassel's method [2] 0.5 gram potassium bromate is mixed with 10 to 50 cc. of the cyanide solution and concentrated sulphuric acid added gradually with constant agitation until reaction commences. When the reaction stops, saturated solution of stannous chloride is added dropwise until the liquid is just colorless. The tint produced is compared with that from a standard gold solution treated in the same manner.

Moir's Method. By Moir's method [3] a measured quantity of the cyanide solution is oxidized by addition of 1 to 2 grams of sodium peroxide and boiling. If sufficient sodium peroxide is present, the brown spot produced by addition of a few drops of lead acetate will immediately dissolve. The lead-aluminum couple formed by addition of aluminum powder precipitates gold which is filtered off. To the aqua regia solution of the precipitate a solution of stannous chloride is added drop by drop until the liquid is dissolved. The purple of Cassius tint developed is compared with permanent standards composed of mixtures of solutions of copper sulphate and cobalt nitrate which have been adjusted to shades corresponding to those produced by known amounts of gold treated according to the method described.

Bettel [4] filters suspended matter from the cyanide solution, adds a measured quantity of a strong solution of potassium cyanide which contains some cuprous cyanide and precipitates gold by the copper zinc couple produced by addition of a measured quantity of zinc fume. The remainder of the method is the same as Prister's.

[1] Proc. Chem. Met. and Min. Soc. of So. Af., IV, 235, 1904.
[2] Eng. and Min. Journal, Oct. 31, 1903.
[3] Proc. Chem. Met. and Min. Soc. of So. Af., Sept., 1913.
[4] Min. World, **33**, 102 and **35**, 987.

Dowsett's [1] factory test of barren cyanide solutions is capable of detecting variation in gold value of 1 cent per ton in solutions varying from one cent to about 15 cents per ton. To 500 cc. of the sample in a bottle with slight shoulder are added 10-15 cc. saturated sodium cyanide solution, 2 or 3 drops saturated lead nitrate solution and 1-2 grams 200-mesh fine zinc dust. The stoppered bottle is shaken violently until the precipitate settles rapidly. Inverting the bottle allows the precipitate to settle into a casserole. Clear liquid is removed by decantation. Zinc is dissolved by hydrochloric acid added drop by drop until reaction ceases. A few drops excess hydrochloric acid and 3–5 drops dilute nitric acid (sp.gr. 1.18) are added and the liquid concentrated to 1–2 cc. The solution is transferred to a ½-in. diameter test-tube, about 1 cc. of stannous chloride reagent added and grade of cyanide solution estimated by the tint obtained after one or two minutes standing. 1/1000 oz. gold per ton of original cyanide solution gives a very slight coloration; 15/10000 a slight yellow; 1/500 a slight pinkish yellow; 3/1000 a strong pink; 1/250 the purple of Cassius. Too much nitric acid hinders the production and the presence of mercury causes modification of the color. No more lead nitrate should be used than is sufficient to produce a rapidly settling precipitate. The stannous chloride reagent is a water solution containing about 12½% crystals and 10% concentrated hydrochloric acid.

PREPARATION OF PROOF GOLD

Commercial gold may contain arsenic, antimony, selenium, tellurium, copper, lead, mercury, silver, zinc, palladium, platinum and other metals of the platinum group. The method of making pure gold depends to a certain extent upon the character and quantity of impurities.[2] The method described assumes the raw material to be of extreme impurity. The metal is treated in 10-g am portions.

When the metal contains silver its solution is effected most quickly by rolling extremely thin and annealing before treatment with acids.

The strips, in a covered No. 6 casserole on a steam bath, are dissolved with a mixture of 5 cc. nitric and 50 cc. hydrochloric acid. If but little silver is present the quantity of hydrochloric acid may be decreased to 25 cc. The solution is evaporated to dryness and the casserole gently heated over a Bunsen flame until all the gold is reduced to metal.

Digestion with ammonia will dissolve most of the silver and copper. After decanting the ammoniacal solution and washing with water, the gold is digested with hot nitric acid. If the solution is wine colored the digestion is continued for several hours, and reheated with fresh portions of acid until the absence of color indicates removal of palladium. The gold is now dissolved with 5 cc. of nitric and 15 to 20 cc. hydrochloric acids, evaporated to dryness, residue moistened with the least quantity of hydrochloric acid, dissolved with about 800 cc. water and liquid transferred to a 1000 cc. beaker. After the faint cloud of silver chloride settles to the bottom of the beaker, the clear liquid only is siphoned to another beaker, and allowed to stand another period of several days if it appears at all cloudy. The clear liquid is now siphoned into a 1000-cc. flask and sulphur dioxide gas passed until the gold is practically all precipitated. The gold is allowed to

[1] Trans. I.M.M., 1912–13, 190; Met. and Chem. Eng., July, 1914.

[2] Eng. and Min. Jour., 68, 785, 1899; "Metallurgy of Gold," Rose, 5th Ed.; Min. and Sci. Press, Nov. 14, 1903; "Manual of Fire Assaying," Fulton; "Assaying of Precious Metals," Smith.

settle, digested with hot nitric acid for a few minutes, washed by decantation several times, redissolved with aqua regia, solution transferred to a casserole, and nitric acid expelled by repeated evaporation to syrup with addition of hydrochloric acid. The product of the second evaporation is moistened with the least quantity of hydrochloric acid, dissolved with water and solution transferred to a 1000-cc. beaker or Erlenmeyer flask. To the liquid of about 500-cc. volume is added 11 grams of ammonium oxalate crystals. The beaker is permitted to remain on a steam bath until reaction is complete. The spongy mass of gold is now washed with hot water by decantation until free of salts.

The gold is dried, melted in a clay crucible which has previously been thinly glazed with borax glass and poured out into a mold of charcoal, graphite and clay or iron polished with graphite.

The ingot, which will have a volume of half a cubic centimeter, is cleaned by paring with a knife and rolled or hammered into a thin sheet. The rolls or hammer should be clean, bright and free of grease.

The gold, cut into convenient strips, is digested for several hours with hydrochloric acid and finally washed thoroughly with distilled water.

The dried gold thus prepared may be considered 1000 fine.

IODINE

WILFRED W. SCOTT

I, *at.wt.* 126.92; *sp.gr.* 4.948[17°]; *m.p.* 113.5°;[1] *b.p.* 184.4° C; *acids*, HI, HIO, HIO_3, HIO_4.

DETECTION

The element may be recognized by its physical properties. It is a grayish black, crystalline solid, with metallic luster, brownish-red in thin layers. It vaporizes at ordinary temperatures with characteristic odor. Upon gently heating the element the vapor is evident, appearing a deep blue when unmixed with other gases, and violet when mixed with air. It colors the skin brown. Chemically it behaves very similarly to chlorine and bromine.

Free iodine colors water yellow to black, carbon disulphide violet, ether or chloroform a reddish color, cold starch solution blue.

Tannin interferes with the usual tests for iodine, unless ferric chloride is present.

Iodide. The dry powder, heated with concentrated sulphuric acid, evolves violet fumes of iodine. Iodine is liberated from iodides by solutions of As^5, Sb^5, Bi^5, Cu″, Fe‴, Cr^6, $H_3Fe(CN)_6$, HNO_2, Cl, Br, H_2O_2, ozone.

Insoluble iodides may be transposed by treatment with H_2S, the filtered solution being tested for the halogen.

Iodate. The acidulated solution is reduced by cold solution of SO_2, or $K_4Fe(CN)_6$, (acidulated with dilute H_2SO_4), or by Cu_2Cl_2, H_3AsO_3, $FeSO_4$, etc. An iodate in nitric acid may be detected by diluting the acid with water, adding starch solution, then hydrogen sulphide water, drop by drop, a blue zone forming in presence of the substance.

ESTIMATION

The element is found free in some mineral waters; combined as iodides and iodates in sea water; in ashes of sea plants; small quantities in a number of minerals, especially in Chili saltpeter as sodium iodate, hence in the mother liquor from the Chilian niter works from which iodine is principally produced. Sea-weed ash (drift kelp, Laminaria digitata and L. stenophylla) is an important source of iodine.

Free iodine, potassium iodide, iodoform, are the principal commercial products.

Preparation and Solution of the Sample

In dissolving the substance it will be recalled that free iodine is soluble in alcohol, ether, chloroform, glycerole, benzole, carbon disulphide, solutions of soluble iodides. One hundred cc. of water at 11° C. is saturated with 0.0182 gram iodine, at 55° with 0.092 gram.

[1] Circular 35 (2d ed.) U. S. Bureau of Standards.

Iodides of silver, copper (cuprous), mercury (mercurous), and lead are insoluble, also TlI, PdI_2. Iodides of other metals are soluble; those of bismuth, tin, and antimony, require a little acid to hold them in solution.

Iodates of silver, barium, lead, mercury, bismuth, tin, iron, chromium require more than 500 parts of water at 15° C. to hold them in solution. Iodates of copper, aluminum, cobalt, nickel, manganese, zinc, calcium, strontium, magnesium, sodium, and potassium are more soluble. One hundred cc. of cold water dissolves 0.00385 gram $AgIO_3$ and 0.000035 gram AgI at ordinary temperatures.

Free Iodine (Commercial Crystals). Iodine is best brought into solution in a strong solution of potassium iodide according to the procedure described for standardization of sodium thiosulphate under Volumetric Methods. The iodine is now best determined volumetrically by titration with standard thiosulphate or arsenic.

Iodine or Iodides in Water. The sample of water is evaporated to about one-fourth its volume and then made strongly alkaline with sodium carbonate. The precipitated calcium and magnesium carbonates are filtered off and washed. The filtrate containing the halogens is evaporated until the salts begin to crystallize out. The hot concentrated solution is poured into three volumes of absolute alcohol and the resulting solution again filtered. The residue is washed four or five times with 95% alcohol. All of the bromine and iodine pass into the solution, whereas a large part of chlorine as sodium chloride remains insoluble and is filtered off. About half a cc. of 50% potassium hydroxide is added and a greater part of the alcohol distilled off with a current of air. The residue is concentrated to crystallization and again poured into three times its volume of absolute alcohol and filtered as above directed. This time only one or two drops of potassium solution is added and the procedure repeated several times. The final filtrate is freed from alcohol by evaporation, the solution taken to dryness and gently ignited, then taken up with a little water and filtered. Iodine is determined in the filtrate, preferably by the volumetric procedure III, decomposition with nitrous acid, described under Volumetric Methods, p. 206.

Organic Substances. If only an iodide is present, the Carius method is followed; in presence of other halogens, the "lime method" is preferred. Details of these methods are given in the chapter on Chlorine under Preparation and Solution of the Sample, p. 121.

Silver iodide cannot be separated from the glass of the combustion-tube by solution with ammonium hydroxide as is the chloride or bromide of silver. The compound, together with the glass, is collected upon a filter paper, and washed with dilute nitric acid, followed by alcohol; then dried at 100° C. After removing most of the iodide and the glass, the filter is ignited in a weighed porcelain crucible, the main bulk of the material then added, the substance fused and weighed as AgI+glass. The mass is then covered with dilute sulphuric acid and a piece of pure zinc added. After several hours (preferably over night) the excess zinc is carefully removed and the iodine solution decanted from the glass and metallic silver, and the residue washed by decantation. The silver is now dissolved in hot dilute nitric acid, then filtered from the residue of glass through a small filter. The glass and filter are ignited and weighed. The difference between the two weighings is due to silver iodide.

Minerals. Phosphates. The substance is decomposed by digestion with 1 : 1 sulphuric acid in a flask through which a current of air passes to sweep out

the iodine vapor into a solution of potassium hydroxide, the sample being boiled until all the iodine vapors have been driven into the caustic. Iodates are converted to iodides by reduction with sulphurous acid.

With the iodine content below 0.02%, a 50 to 100-gram sample should be taken.

SEPARATIONS

Separation of Iodine from the Heavy Metals. The heavy metals are precipitated as carbonates by boiling with solutions of alkali carbonates, the soluble alkali iodide being formed.

Iodine is liberated from combination by nitrous acid.

Silver iodide may be decomposed by warming with metallic zinc and sulphuric acid.

Separation of Iodine from Bromine or from Chlorine.[1] Details of separation and estimation of the halides in presence of one another are given in the chapter on Chlorine. Advantage is taken of the action of nitrous acid on dilute solutions, free iodine being liberated, while bromides and chlorides are not acted upon.

The solution containing the halogens is placed in a 1½-liter flask (with round bottom) and diluted to about 700 cc. Through a two-holed stopper a glass tube passes to the bottom of the flask; through this tube steam is conducted to assist the volatilization of iodine. A second short tube connected to the absorption apparatus conducts the evolved vapor from the flask into a 5% caustic soda solution containing an equal volume of hydrogen peroxide (about 50 cc. of each). The absorption system may be made by connecting two Erlenmeyer flasks in series, the inlet tubes dipping below the solutions in the flasks. It is advisable to cool the receivers with ice.

Five to 10 cc. of dilute sulphuric acid (1 : 5) and 10 cc. of 10% sodium nitrite solution are added to the liquid containing the halogens, the apparatus is immediately connected, and the contents of the large flask heated to boiling, conducting steam into it at the same time. The iodine vapor is gradually driven over into the cooled receiving flasks.

When the solution in the large flask has become colorless it is boiled for twenty minutes longer. The steam is now shut off, the flask disconnected from the receiving flasks and the heat turned off. The contents of the receiving flasks are combined with the washing from the connecting tubes and the solution heated to boiling to remove the excess of hydrogen peroxide. The cooled liquid is acidified with a little sulphuric acid and the solution decolorized with a few drops of sulphurous acid. Iodine is now precipitated as silver iodide by adding an excess of silver nitrate and a little nitric acid and boiling the mixture to coagulate the precipitate. The precipitate is filtered through a Gooch crucible and weighed as usual.

Chlorine and bromine remain in the large flask in combined form and may be determined in this solution if desired.

NOTES. *Reaction:* $2NaOH + 2I = NaI + NaOI + H_2O$ and $NaOI + H_2O_2 = H_2O + O_2 + NaI$.

Consult Separations in the chapter on Chlorine, p. 123.

[1] Method of Jannasch, Zeit. für anorg. Chem., 1, p. 144. Ibid, Prakt. Leit. der Gewichts-analyse, p. 182, et seq.

Separation of Iodine from Chlorine and Bromine by Precipitation as Palladous Iodide. The solution containing the halogens is acidified with hydrochloric acid, and palladous chloride solution added to the complete precipitation of the iodide. The compound is allowed to settle in a warm place for twenty-four hours or more and then filtered and washed free of the other halogens. It may now be dried and weighed as palladous iodide, PdI_2, or ignited in a current of hydrogen, then weighed as metallic palladium and the equivalent iodine calculated. See Gravimetric methods.

GRAVIMETRIC METHODS

Precipitation as Silver Iodide

The procedure is practically the same as that described for determining chlorine.

Silver nitrate solution is added to the iodide solution, slightly acidified with nitric acid. The precipitate is filtered into a weighed Gooch crucible, then washed, dried, gently ignited, and weighed as silver iodide.

$$AgI \times 0.5406 = I \text{ or } \times 0.7071 = KI.$$

NOTE. If filter paper is used in place of a Gooch crucible, the precipitate is removed and the filter ignited separately. A few drops of nitric and hydrochloric acid are added, the acids expelled by heat and the residue weighed as AgCl. This, multiplied by $1.638 = AgI$. The result is added to the weight of the silver iodide, which is ignited and weighed separately.

Determination of Iodine as Palladous Iodide

This method is applicable for the direct determination of iodine in iodides in presence of other halogens.

The method of isolation of iodine as the palladous salt has been given under Separations. The salt dried at 100° C. is weighed as PdI_2.

$$PdI_2 \times 0.704 = I.$$

PdI_2 ignited in a current of hydrogen is changed to metallic palladium.

$$Pd \times 2.379 = I.$$

VOLUMETRIC METHODS

Determination of Hydriodic Acid—Soluble Iodides

Free hydriodic acid cannot be determined by the usual alkalimetric methods for acids. The procedures for its estimation, free or combined as a soluble salt, depends upon the liberation of iodine and its titration with standard sodium thiosulphate, in neutral or slightly acid solution; or by means of standard arsenious acid, in presence of an excess of sodium bicarbonate in a neutral solution. The following equations represent the reactions that take place:

I. Thiosulphate. $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

II. Arsenite. $Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$.

The free acid formed in the second reaction is neutralized and the reversible reaction thus prevented:

$$HI+NaHCO_3=NaI+H_2O+CO_2.$$

The presence of a free alkali is not permissible, as the hydroxyl ion would react with iodine to form iodide, hypoiodite and finally iodate, hence sodium or potassium carbonates cannot be used. Alkali bicarbonates, however, do not react with iodine.

Standard Solutions. ***Tenth Normal Sodium Thiosulphate.*** From the reaction above it is evident that 1 gram molecule of thiosulphate is equivalent to 1 atom iodine = 1 atom hydrogen, hence a tenth normal solution is equal to one-tenth the molecular weight of the salt per liter, e.g., 24.822 grams $Na_2S_2O_3\cdot 5H_2O$; generally a slight excess is taken—25 grams of the crystallized salt. It is advisable to make up 5 to 10 liters of the solution, taking 125 to 250 grams sodium thiosulphate crystals and making up to volume with distilled water, boiled free of carbon dioxide. The solution is allowed to stand a week to ten days, and then standardized against pure, resublimed iodine.

About 0.5 gram of the purified iodine is placed in a weighing bottle containing a known amount of saturated potassium iodide solution (2 to 3 grams of KI free from KIO_3 dissolved in about ½ cc. of H_2O), the increased weight of the bottle, due to the iodine, being noted. The bottle and iodine are placed in a beaker containing about 200 cc. of 1% potassium iodide solution (1 gram KI per 200 cc.), the stopper removed with a glass fork and the iodine titrated with the thiosulphate to be standardized.

Calculation. The weight of the iodine taken, divided by the cc. thiosulphate required, gives the value of 1 cc. of the reagent; this result divided by 0.012692 gives the normality factor.

NOTE. The thiosulphate solution may be standardized against iodine, which has been liberated from potassium iodide in presence of hydrochloric acid by a known amount of standard potassium bi-iodate, a salt which may be obtained exceedingly pure.

$$KIO_3\cdot HIO_3+10KI+11HCl=11KCl+6H_2O+6I_2.$$

A tenth normal solution contains 3.2496 grams of the pure salt per liter. (One cc. of this will liberate 0.012692 gram of iodine from potassium iodide.) The purity of the salt should be established by standardizing against thiosulphate, which has been freshly tested against pure resublimed iodine.

About 5 grams of potassium iodide (free from iodate) are dissolved in the least amount of water that is necessary to effect solution, and 10 cc. of dilute hydrochloric acid (1 : 2) are added, and then 50 cc. of the standard bi-iodate solution. The solution is diluted to about 250 cc. and the liberated iodine titrated with the thiosulphate reagent; 50 cc. will be required if the reagents are exactly tenth normal.

Tenth Normal Arsenite. From the second reaction above it is evident that As_2O_3 is equivalent to $2I_2$, e.g., to 4H, hence ¼ the gram molecular weight of arsenious oxide per liter will give a normal solution: $198\div 4=49.5$.

4.95 grams of pure arsenious oxide is dissolved in a little 20% sodium hydroxide solution, the excess of the alkali is neutralized with dilute sulphuric acid, using phenolphthalein indicator, the solution being just decolorized. Five hundred cc. of distilled water containing about 25 grams of sodium bicarbonate are added. If a pink color develops, this is destroyed with a few drops of weak sulphuric acid. The solution is now made to volume, 1000 cc. The

reagent is standardized against a measured amount of pure iodine. The oxide may be dissolved directly in sodium bicarbonate solution.

NOTE. Commercial arsenious oxide is purified by dissolving in hot hydrochloric acid, filtering the hot saturated solution, cooling, decanting off the mother liquor, washing the deposited oxide with water, drying and finally subliming.

Starch Solution. Five grams of soluble starch are dissolved in cold water, the solution poured into 2 liters of hot water and boiled for a few minutes. The reagent is kept in a glass-stoppered bottle.

Iodides are decomposed and iodine determined by one of the following procedures:

I. Decomposition of the Iodide by Ferric Salts

The method takes advantage of the following reaction:

$$Fe_2(SO_4)_3 + 2KI = K_2SO_4 + I_2 + 2FeSO_4.$$

The procedure enables a separation from bromides, as these are not acted upon by ferric salts.

Procedure. To the iodide in a distillation flask is added an excess of ferric ammonium alum, the solution acidified with sulphuric acid, then heated to boiling, and the iodine distilled into a solution of potassium iodide. The free iodine in the distillate is titrated with standard thiosulphate, or by arsenious acid in presence of an excess of sodium bicarbonate.

The reagent is added from a burette until the titrated solution becomes a pale yellow color. About 5 cc. of starch solution are now added and the titration continued until the blue color of the starch fades and the solution becomes colorless.

One cc. of tenth normal reagent = 0.012692 gram iodine, equivalent to 0.012793 gram HI, or 0.016602 gram KI.

II. Decomposition with Potassium Iodate [1]

The reaction with potassium iodate is as follows:

$$5KI + KIO_3 + 6HCl = KCl + 3H_2O + 3I_2.$$

It is evident that $\frac{5}{6}$ of the titration for iodine would be equal to the iodine of the iodide, hence 1 cc. of tenth normal thiosulphate is equivalent to $0.012692 \times \frac{5}{6} = 0.01058$ gram iodine due to the iodide. The procedure is as follows:

Procedure. A known amount of tenth normal potassium iodate is added to the iodide solution, in sufficient amount to liberate all of the iodine, combined as iodide, and several cc. in excess. Hydrochloric acid and a piece of calcite are added. The mixture is boiled until all of the liberated iodine has been expelled. To the cooled solution 2 or 3 grams of potassium iodide are added and the liberated iodine, corresponding to the excess of iodate in the solution, is titrated with standard thiosulphate. If 1 cc. of thiosulphate is equal to 1 cc. of the iodate, then the total cc. of the iodate used, minus the cc. thio-

[1] H. Dietz and B. M. Margosches, Chem. Ztg., 2, 1191, 1904. Treadwell and Hall, "Analytical Chemistry," Vol. 2.

sulphate required in the titration gives a difference due to the volume of iodate required to react with the iodide of the sample.

One cc. of N/10 KIO_3 = 0.01058 gram I in KI.

NOTE. Tenth normal potassium iodate contains 3.5675 grams KIO_3 per 1000 cc.

III. Decomposition of the Iodide with Nitrous Acid (Fresenius)

Nitrous acid reacts with an iodide as follows:

$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2.$$

Since neither hydrochloric nor hydrobromic acids are attacked by nitrous acid, the method is applicable to determining iodine in presence of chlorine and bromine; hence is useful for determining small amounts of iodine in mineral waters containing comparatively large amounts of the other halogens.

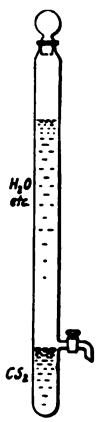


FIG. 39.

Nitrous Acid. The reagent is prepared by passing the gas into strong sulphuric acid until saturated.

Procedure. The neutral or slightly alkaline solution of the iodide is placed in a glass-stoppered tube or small flask and slightly acidified with dilute sulphuric acid, a little freshly distilled colorless carbon disulphide (or chloroform) added, then 10 drops of nitrous acid reagent. The mixture is well shaken and the disulphide allowed to settle. The supernatant solution is poured into another similar container and extracted with a fresh portion of disulphide. The solution is poured onto a moistened filter and the disulphide, if discolored, is added to the first extract. The combined extracts are washed with three or four portions of water, then transferred to the filter and again washed until free from acid. A hole is made in the filter and the disulphide allowed to run into a small beaker and the filter washed down with about 5 cc. of water. Three cc. of 5% sodium bicarbonate are added and the iodine titrated with N/20 or N/50 standard thiosulphate, the reagent being added until the reddish-violet carbon disulphide becomes colorless.

The sodium thiosulphate used is standardized against a known amount of pure potassium iodide treated in the manner described above.

One cc. N/20 $Na_2S_2O_3$ = .00635 gram I, 1 cc. N/50 $Na_2S_2O_3$ = .002538 gram I.

NOTE. If the extracted aqueous solution appears yellow, it must be again treated with additional carbon disulphide until all the iodine has been removed (e.g., until additional CS_2 is no longer colored when shaken with the solution).

Treadwell and Hall recommend a specially designed glass-stoppered tube with stop-cock for this determination, Fig. 39. The stop-cock is so arranged that the supernatant liquid may be readily drawn off from the disulphide.[1]

[1] Treadwell and Hall, "Analytical Chemistry," Vol. 2, p. 657, 3d Ed.

IV. Liberation of Iodine by Means of Hydrogen Peroxide and Phosphoric Acid [1]

Principle. Iodine is liberated from an iodide by addition of hydrogen peroxide to the solution acidified with phosphoric acid, the iodine distilled into potassium iodide and titrated with thiosulphate.

Procedure. Fifty cc. of the iodide solution are mixed with 5 cc. of pure phosphoric acid and 10 to 20 cc. hydrogen peroxide added, the mixture being placed in a round-bottomed flask, connected with a short condenser, delivering into two absorption vessels containing a 10% solution of potassium iodide. A current of air is drawn through the apparatus, and the contents of the flask gradually heated to boiling. The iodine is absorbed in the potassium iodide solution and titrated as usual with standard sodium thiosulphate. Twenty minutes' heating is generally sufficient.

One cc. $Na_2S_2O_3$ = 0.012692 gram I, or 0.016602 gram KI.

NOTE. Iodine in urine may be determined by evaporating to 1/10 its volume. After adding an excess of sodium hydroxide, the mixture is taken to dryness and gently ignited. The ash may be used for the iodine determination.

V. Oxidation of Combined Iodine with Chlorine. (Mohr's Modification of Dupré's Method)[2]

When a solution of potassium iodide is treated with successive amounts of chlorine water, iodine is liberated, which reacts with an excess of chlorine with formation of chloride of iodine (ICl) and with greater excess the pentachloride (ICl_5) which is changed in presence of water to iodic acid (HIO_3).

Procedure. The weighed iodide compound is brought into a stoppered flask, and chlorine water delivered from a large burette until all yellow color has disappeared. A drop of the mixture brought in contact with a drop of starch solution should produce no blue color. Sodium bicarbonate is now added until the mixture is slightly alkaline, followed by an excess of potassium iodide and 4 to 5 cc. of starch reagent. Standard thiosulphate is now added until the blue color is removed. The excess of chlorine water is thus ascertained. From the value of the chlorine reagent the iodine of the sample may readily be calculated.

The chlorine water is standardized by running 25 to 50 cc. of the reagent into potassium iodide solution (see procedure for bromides, p. 81), and titrating the liberated iodine with standard sodium thiosulphate. The value of the reagent in terms of thiosulphate are thus ascertained and from this the value per cc. in terms of iodine.

OTHER METHODS

Volhard's Method for Determining Iodides

This procedure is very similar to those for determining chlorine or bromine, with the exception that silver iodide formed will occlude both the iodide solu-

[1] E. Winterstein and E. Herzfeld, Zeit. Physiol. Chem., **63**, 49–51, 1909. Chem. Zentralbl., (1), 473–474, 1910.

[2] Sutton, "Volumetric Analysis," 10th Ed.

tion and silver nitrate unless the additions of the silver salt are made in small portions with vigorous shaking.

Standard silver nitrate is added to the solution in a glass-stoppered flask, shaking vigorously with each addition. As long as the solution appears milky the precipitation is incomplete. When the silver iodide is coagulated and the supernatant liquid appears colorless, ferric alum solution is added, and the excess of silver nitrate titrated with potassium sulphocyanate until the characteristic reddish end-point is obtained.

The iodine is calculated from the amount of silver nitrate required. E.g., total $AgNO_3$ added, minus excess determined by KCNS = cc. $AgNO_3$ required by the iodine.

NOTE. The ferric salt oxidizes hydriodic acid with separation of iodine, whereas the silver iodide is not acted upon, hence the indicator is added after all the iodide has combined with silver.

VI. Determination of Iodates

The procedure is the reciprocal of the one for determination of iodide by means of an iodate:

Reaction. $KIO_3+5KI+6HCl=6KCl+3H_2O+3I_2$.

Procedure. The solution containing the iodate is allowed to run into an excess of potassium iodide solution containing hydrochloric acid. The liberated iodine is titrated with sodium thiosulphate as usual.

One cc. N/10 $Na_2S_2O_3$ = 0.002932 gram HIO_3, or 0.003567 gram KIO_3.

VII. Determination of Periodates

The procedure is the same as that described for iodates, the reaction in this case, however, being as follows:

$$KIO_4+7KI+8HCl=8KCl+4H_2O+4I_2.$$

From the equation it is evident that 1 gram molecule of the iodate is equivalent to 8 atoms of iodine = 8 atoms of hydrogen, hence $\frac{1}{8}$ the molecular weight per liter of solution would equal a normal solution. Therefore, 1 cc. of a tenth normal solution would contain 0.019193 ÷ 8 = 0.002399 gram HIO_4.

One cc. N/10 $Na_2S_2O_3$ = 0.002399 gram HIO_4, or = 0.002849 gram $HIO_4 \cdot 2H_2O$, or = 0.002875 gram KIO_4.

VIII. Determination of Iodates and Periodates in a Mixture of the Two

The procedure depends upon the fact that an iodate does not react with potassium iodide in neutral or slightly alkaline solutions, whereas a periodate undergoes the following reactions:

$$KIO_4+2KI+H_2O=2KOH+KIO_3+I_2.$$

Procedure. The sample, dissolved in water, is divided into two equal portions.

A. To one portion a drop of phenolphthalein indicator is added and the

solution made just faintly alkaline by addition of alkali to acid solutions or hydrochloric acid to alkaline solution, as the case may require. Ten cc. of cold saturated solution of sodium bicarbonate are added and an excess of potassium iodide. The liberated iodine is titrated with tenth normal arsenious acid.[1] ($Na_2S_2O_3$ will not do in this case, as the solution is alkaline.)

One cc. N/10 As_2O_3 = 0.0115 gram KIO_4.

B. To the other portion potassium iodide is added in excess and the solution made distinctly acid. The liberated iodine is titrated with standard sodium thiosulphate.[2] (As_2O_3 will not do.)

Calculation. In the acid solution, *B*, both iodates and periodates are titrated, whereas in the alkaline solution, *A*, only the periodates are affected. From the reactions in VII and VIII it is evident that 1 cc. $Na_2S_2O_3$ = 4 cc. As_2O_3 for the periodate titration, hence

Cc. $Na_2S_2O_3$ − cc. $As_2O_3 \times 4$ = cc. thiosulphate due to KIO_3.

The difference, multiplied by 0.003567 = grams KIO_3 in the sample.

[1] In alkaline solutions the arsenious acid titration must be made, whereas in acid solutions potassium thiosulphate is used.

[2] E. Müller and O. Freedburger, Ber., 2655, 1902.

IRON

WILFRED W. SCOTT

Fe, *at.wt.* 55.84; *sp.gr.* 7.85–7.88; *m.p. pure* 1530°,[1] *wrought* 1600°,[2] *white pig* 1075°,[1] *gray pig* 1275°,[1] *steel* 1375°;[1] *b.p.* 2450°[1] C.; *oxides* FeO, Fe_2O_3, Fe_3O_4.

DETECTION

Ferric Iron. The yellow to red color in rocks, minerals, and soils is generally due to the presence of iron.

Hydrochloric acid solutions of iron as ferric chloride are colored yellow.

Potassium or ammonium sulphocyanate produces a red color with solutions containing ferric iron. Nitric acid and chloric acid also produce a red color with potassium or ammonium sulphocyanate. This color, however, is destroyed by heat, which is not the case with the iron compound. The red color of ferric iron with the cyanate is destroyed by mercuric chloride and by phosphates, borates, certain organic acids, and their salts, e.g., acetic, oxalic, tartaric, citric, racemic, malic, succinic, etc.

Potassium ferrocyanide, $K_4Fe(CN)_6$, produces a deep blue color with ferric salts.

Salicylic acid added to the solution of a ferric salt containing no free mineral acid gives a violet color. Useful for detecting iron in alum and similar products.

Ferrous Iron. Potassium Ferricyanide, $K_3Fe(CN)_6$, gives a blue color with solutions of ferrous salts.

Distinction between Ferrous and Ferric Salts.

KCNS gives red color with Fe‴ and no color with Fe″.

$K_4Fe(CN)_6$ gives a blue color with Fe″ and a brown or green with Fe‴.

NH_4OH, NaOH or **KOH** precipitates red, $Fe(OH)_3$ with Fe‴ and white, $Fe(OH)_2$ with Fe″ turning green in presence of air due to oxidation.[3]

Sodium peroxide produces a reddish-brown precipitate of $Fe(OH)_3$ with either ferrous or ferric salt solutions, the former being oxidized to the higher valence by the peroxide. Chromium and aluminum remain in solution, if present in the sample.

ESTIMATION

Iron is so widely diffused in nature that its determination is necessary in practically all complete analyses of ores, rocks, minerals, etc. It is especially important in the evaluation of iron ores for the manufacture of iron and steel. Among the ores of iron the following are more common:

Oxides. Red hematite, Fe_2O_3; brown hematite, $2Fe_2O_3 \cdot 3H_2O$; black magnetite or magnetic iron ore, Fe_3O_4. Ferric oxide with varying amounts of water

[1] Circular 35 (2d Ed.) U. S. Bureau of Standards.

[2] D. Van Nostrand's Chemical Annual.—Olsen.

[3] The green salt is a hydrate of Fe_3O_4. The white precipitate can be obtained in absence of air or by using H_2SO_3 to take up oxygen in solution.

forms the substances known as hematite, göthite, limonite, yellow ochre, bog iron ore.

Sulphide. Iron pyrites or "fool's gold," FeS_2; pyrrhotite, FeS.

Carbonates. Spatic iron ore, $FeCO_3$; combined with clay in clay ironstone with bituminous material as "black band."

Iron is determined in the cinders and in iron ore briquettes from burned iron pyrites, by-products of sulphuric acid.

It is found as an impurity in a large number of commercial salts and in the mineral acids.

Preparation and Solution of the Sample

The material should be carefully sampled and quartered down according to the general procedure for sampling. Ores should be ground to pass an 80-mesh sieve. In analysis of metals, both the coarse and fine drillings are taken.

The following facts regarding solubility should be remembered: The *element* is soluble in hydrochloric acid and in dilute sulphuric acid, forming ferrous salts with liberation of hydrogen. It is insoluble in concentrated, cold sulphuric acid, but is attacked by the hot acid, forming ferric sulphate with liberation of SO_2. Moderately dilute, hot nitric acid forms ferric nitrate and nitrous oxide; the cold acid gives ferrous nitrate and ammonium nitrate or nitrous oxide or hydrogen. Cold, concentrated nitric acid forms "passive iron," which remains insoluble in the acid. The *oxides of iron* are readily soluble in hydrochloric acid, if not too strongly ignited, but upon strong ignition the higher oxides dissolve with extreme difficulty. They are readily soluble, however, by fusion with acid potassium sulphate followed by an acid extraction. *Silicates* are best dissolved by hot hydrochloric acid containing a few drops of hydrofluoric acid or by fusion with sodium and potassium carbonates, followed by hot hydrochloric acid.

Soluble Iron Salts. Water solutions are acidified with HCl or H_2SO_4, so as to contain about 3% of free acid.

Ores. The samples should be pulverized to pass an 80- to 100-mesh sieve.

Sulphides, Ores Containing Organic Matter. One- to 5-gram samples should be roasted in a porcelain crucible over a Bunsen flame for about half an hour, until oxidized. The oxide is now dissolved as directed in the following procedure.

Oxides, Including Red and Brown Hematites, Magnetic Iron Ore, Spatose Iron Ore, Roasted Pyrites, and Iron Ore Briquettes. One to 5 grams of the ore, placed in a 400-cc. beaker, is dissolved by adding twenty times its weight of strong hydrochloric acid with a few drops of 5% stannous chloride solution. Addition of 4 or 5 drops of HF is advantageous if small amounts of silica are present. The solution is covered with a watch-glass and heated to 80 or 90° C. until solution is complete. Addition of more stannous chloride may be necessary, as this greatly assists solution. An excess sufficient to completely decolorize the solution necessitates reoxidation with hydrogen peroxide, hence should be avoided. If a colored residue remains, it should be filtered off, ignited and fused with a mixture of Na_2CO_3 and K_2CO_3 in a platinum crucible. The fusion dissolved in dilute HCl is added to the main filtrate.

NOTE. The ore placed in a porcelain boat in a red-hot combustion tube may be reduced with hydrogen (taking precaution first to sweep out oxygen with CO_2) and after cooling in an atmosphere of hydrogen the reduced iron may be dissolved in acid and titrated.

Iron Silicates. One to 5 grams of the material, placed in a deep platinum crucible, is treated with ten times its weight of 60% HF and 3 to 4 drops of conc. H_2SO_4. The mixture is evaporated to near dryness on the steam bath and taken up with dilute sulphuric acid or hydrochloric acid. The latter acid is the best solvent for iron.

Fusion with Potassium Bisulphate. The sample is mixed with ten times its weight of the powdered bisulphate and 2–3 cc. of concentrated sulphuric acid added. A porcelain or silica dish will do for this fusion. The fusion should be made over a moderate flame and cooled as soon as the molten liquid becomes clear. Complete expulsion of SO_3 should be avoided. It may be necessary to cool and add more conc. sulphuric acid to effect solution. Iron and alumina completely dissolve, but silica remains undissolved. The melt is best cooled by pouring it on a large platinum lid.

Fusion with Carbonates of Sodium and Potassium. The residues insoluble in hydrochloric acid are fused with 5 parts by weight of the fusion mixture ($Na_2CO_3+K_2CO_3$) in a platinum crucible. The Méker blast will be necessary. When the effervescence has ceased and the melt has become clear, the crucible is removed from the flame, a platinum wire inserted and the melt cooled. Upon gently reheating, the fuse may be readily removed by the wire in a convenient form for solution in dilute hydrochloric acid.

The bisulphate fusion is recommended for fusion of residues high in iron and alumina. It is an excellent solvent for ignited oxides of these elements. The carbonate fusions are adapted to residues containing an appreciable amount of silica.

Iron and steel are best dissolved in hydrochloric acid with a few drops of nitric acid. The iron hydroxide should be precipitated or the solution taken to dryness to expel the nitric acid followed by resolution in dilute hydrochloric acid or sulphuric acid.

The finer the material the more rapid its solution is a fact that should be remembered in all cases.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRON

The gravimetric determination of iron may be made from solutions practically free from other metals. A number of elements such as phosphorus, arsenic, molybdenum, tungsten, vanadium, and the like, form fairly stable compounds with iron in neutral or slightly alkaline solutions, whereas others, such as lead, copper, nickel, cobalt, sodium, and potassium may be occluded in the ferric hydrate precipitate and are removed only with considerable difficulty. Aluminum, chromium, and several of the rare earths are precipitated with iron, if present. These facts taken into consideration, the volumetric methods are generally preferred as being more rapid and trustworthy.

Determination of Iron as Fe_2O_3

Iron is precipitated as the hydroxide and ignited to the oxide, Fe_2O_3, in which form it is weighed.

Reactions. $FeCl_3+3NH_4OH=Fe(OH)_3+3NH_4Cl.$
$2Fe(OH)_3+\text{heat}=Fe_2O_3+3H_2O.$

Procedure. One-gram sample or a larger amount of material if the iron content is low, is brought into solution with hydrochloric acid, aqua regia, or by fusion with potassium carbonate or potassium acid sulphate, as the case may require. Silica is filtered off and the acid solution gassed with H_2S if members of that group are present. The filtrate is boiled to expel H_2S and the iron oxidized to ferric condition by boiling with 5 cc. concentrated nitric acid.

Absence of Aluminum and Chromium. About 1 gram of ammonium chloride salt or its equivalent in solution is added, the volume made to about 200 cc. and ammonium hydroxide added in slight excess to precipitate $Fe(OH)_3$. The solution is boiled for about five minutes, then filtered through an ashless filter. (S. & S. 589 is good for this purpose.)

If Aluminum and Chromium are Present. In place of ammonium hydroxide powdered sodium peroxide is added in small portions until the precipitate first formed clears, the solution being cold and nearly neutral. It is diluted to about 300 cc. and boiled ten to fifteen minutes to precipitate the iron. Aluminum and chromium are in solution. (Mn will precipitate with Fe, if present.) The precipitate is filtered onto a rapid filter and washed with hot water.

Second Precipitation. In either case dissolve the precipitate with the least amount of hot dilute hydrochloric acid and wash the paper free of iron. Add a few cc. of 10% ammonium chloride solution and reprecipitate the hydroxide of iron by adding an excess of ammonium hydroxide, the volume of the solution being about 200 cc. Washing the precipitate by decantation is advisable. Three such washings, 100-cc. portions, followed by two or three on the filter paper, will remove all impurities.

Ignition. The precipitate is ignited wet over a low flame, gradually increasing the heat. Blasting is not recommended, as the magnetic oxide of iron, Fe_3O_4, will form with high heating. The oxide heated gently appears a reddish-brown. Higher heat gives the black oxide, Fe_3O_4. Twenty minutes' ignition, at red heat, is sufficient.

The crucible, cooled in a desiccator, is weighed and Fe_2O_3 obtained.

Factors. $Fe_2O_3 \times 0.6994 = Fe.$
$Fe_2O_3 \times 0.8998 = FeO.$

Precipitation of Iron with "Cupferron," Amino nitrosophenyl-hydroxylamine [1]

By this procedure iron may be precipitated directly in acid solution in presence of a number of elements. Mercury, lead, bismuth, tin, and silver may be partially precipitated. Copper precipitates with iron, but may be easily removed by dissolving it out with ammonia. The method is especially adapted for separation of iron from aluminum, nickel, cobalt, chromium, cadmium, and zinc.

Procedure. The solution containing the iron is made up to 100 cc. and 20 cc. of concentrated hydrochloric acid added. To this cool solution (room temperature) Baudisch's reagent, cupferron, is slowly added with constant stirring, until no further precipitation of iron takes place, and crystals of the reagent appear. The iron precipitate is a reddish-brown. Copper gives a grayish-white flocculent compound. An excess of the reagent equal to one-fifth of the volume of the solution is now added, the precipitate allowed to settle for about fifteen minutes, then poured into a filter paper and washed, first with 2N. HCl, followed by water, then with ammonia and finally with water. The drained precipitate is slowly ignited in a porcelain or platinum crucible and the residue weighed as Fe_2O_3.

$$Fe_2O_3 \times 0.6994 = Fe.$$

NOTES. Baudisch's reagent, amino nitrosophenyl-hydroxylamine (cupferron), is made by dissolving 6 grams of the salt in water and diluting to 100 cc. The reagent keeps for a week if protected from the light. It decomposes in the light, forming nitrobenzine. Turbid solutions should be filtered.

The precipitates of copper or iron are but slowly attacked by twice normal hydrochloric acid in the cold, but decomposed by hot acid, hence the solution and reagent should be cold.

Cold, dilute potassium carbonate solution, or ammonium hydroxide, have no action on the iron precipitate; the copper compound dissolves readily in ammonia. Alkaline hydroxide causes rapid decomposition.

The precipitation is best made in comparatively strong acid solutions (HCl, H_2SO_4, or acetic acid).

VOLUMETRIC DETERMINATION OF IRON IN ORES AND METALLURGICAL PRODUCTS

General Considerations. Two general procedures are commonly employed in the determination of iron.

A. Oxidation of ferrous to ferric condition by standard oxidizing agents.

B. Reduction of ferric iron to ferrous condition.

The sample is dissolved as directed under Preparation and Solution of the Sample.

[1] O. Baudisch, Chem. Ztg., **33**, 1298, 1905. Ibid., **35**, 913, 1911. O. Baudisch and V. L. King, Jour. Ind. Eng. Chem., **3**, 627, 1911.

Determination of Iron by Oxidation Methods

Some modification of either the dichromate or permanganate methods is commonly employed in the determination of iron by oxidation. To accomplish this quantitatively, the iron must be reduced to its ferrous condition. This may be accomplished in the following ways:

1. Reduction by Hydrogen Sulphide. During the course of a complete analysis of an ore, H_2S is passed into the acid solution to precipitate the members of that group (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Pt, Au, Se, etc.). The filtrate contains iron in the reduced condition suitable for titration with either dichromate or permanganate, the excess of H_2S having been boiled off. If the expulsion of H_2S is conducted in an Erlenmeyer flask there is little chance for reoxidation of the iron during the boiling. Reduction by H_2S is very effective and is frequently advisable. This is the case when titanium is present, since this is not reduced by H_2S, but by methods given below. Arsenic, antimony, copper, and platinum, which, if present would interfere, are removed by this treatment.

Reaction. $2FeCl_3+H_2S=2FeCl_2+2HCl+S.$

2. Reduction with Stannous Chloride. $SnCl_2$ solution acts readily in a hydrochloric acid solution of the ore; the reduction of the iron is easily noted by the disappearance of the yellow color. The excess of the reagent is oxidized to $SnCl_4$ by addition of $HgCl_2$.

Reactions. 1. $2FeCl_3+SnCl_2=2FeCl_2+SnCl_4.$
2. Excess $SnCl_2+2HgCl_2=SnCl_4+2HgCl$ precipitated.

An excess of $SnCl_2$ is advisable, but a large excess is to be avoided, as a secondary reaction would take place, as follows: $2SnCl_2+2HgCl_2=2SnCl_4+2Hg$. This reaction is indicated by the darkening of the solution upon the addition of $HgCl_2$. Precipitation of metallic mercury would vitiate results. The solution should be cooled before addition of mercuric chloride. About 15–20 cc. of saturated mercuric chloride, $HgCl_2$, solution should be sufficient.

3. Reduction by a Metal such as Test Lead, Zinc, Magnesium, Cadmium, or Aluminum, in Presence of Either Hydrochloric Acid or Sulphuric Acid. The former acid is preferred with the dichromate titration, and the latter with the permanganate. Two methods of metallic reduction are in common use—reduction by means of test lead, and reduction with amalgamated zinc by means of the Jones reductor.

(*a*) **Reduction with Test Lead.** By this method copper is precipitated from solution and small amounts of arsenic and antimony expelled. Sufficient test lead is added to the acid ferric solution to completely cover the bottom of the beaker. The solution is covered and boiled vigorously until the yellow color has completely disappeared, and the solution is colorless. The reduced iron solution, cooled, is decanted into a 600-cc. beaker, the remaining iron washed out from the lead mat by several decantations with water; two or three 50-cc. portions of water should be sufficient; the washings are added to the first portion. If the solution becomes slightly colored, a few drops of stannous chloride, $SnCl_2$, solution are added, followed by 10 cc. mercuric chloride, $HgCl_2$, solution. The sample is now ready for titration.

(*b*) **Reduction with Zinc, Using the Jones Reductor.** The acid sol ution of iron, preferably sulphuric acid, is passed through a column of amalgamated zinc.[1] The hydrogen evolved in presence of the zinc reduces the ferric iron to ferrous condition. The procedure is described in detail under the Permanganate Method for Determination of Iron, page 218. Titanium if present will also be reduced.

4. Reduction with Sulphurous Acid, Sodium Sulphite or Metabisulphite. SO_2 gas is passed into a neutral solution of iron, since iron is not reduced readily in an acid solution by this method. The excess SO_2 is expelled by acidifying the solution and boiling.

5. Reduction with potassium iodide, the liberated iodine being expelled by heat.

In the solution of the ore with stannous chloride and hydrochloric acid, if an excess of the former has been accidentally added, it will be necessary to oxidize the iron before reduction. This may be accomplished by addition of hydrogen peroxide until the yellow color of ferric chloride appears (or by addition of $KMnO_4$ *solution), the excess* H_2O_2 *may be removed by boiling. The iron may now be reduced by one of the above methods.*

Volumetric Determination of Iron by Oxidation with Potassium Dichromate

Principle. This method depends upon the quantitative oxidation of ferrous salts in cold acid solution (HCl or H_2SO_4) to ferric condition by potassium dichromate, the following reaction taking place:

$$6FeCl_2+K_2Cr_2O_7+14HCl=6FeCl_3+2CrCl_3+2KCl+7H_2O.$$

Potassium ferricyanide is used as an outside indicator. This reagent produces a blue compound with ferrous salts and a yellowish-brown with ferric. The chromic salt formed by the reaction with iron colors the solution green.

Reagents Required. ***Standard Potassium Dichromate.*** When oxygen reacts with ferrous salts, the following reaction takes place:

$$6FeCl_2+6HCl+3O=6FeCl_3+3H_2O.$$

Comparing this reaction with that of dichromate, it is evident that a normal solution of dichromate contains one-sixth of the molecular weight of $K_2Cr_2O_7$ per liter, namely, 49.033 grams. For general use it is convenient to have two strengths of this solution, N/5 for ores high in iron and N/10 for products containing smaller amounts.

Standardization. For N/5 solution 9.807 grams of the recrystallized dehydrated salt are dissolved and made up to one liter; N/10 potassium dichromate contains 4.903 grams of the pure salt per liter. It is advisable to allow the solution to stand a few hours before standardization. The Sibley iron ore furnished by the U. S. Bureau of Standards, Washington, D. C., is recommended as the ultimate standard. Other ores uniform in iron may be standardized against the Sibley ore and used as standards. The ore in question contains 69.20% Fe (1914). For accurate work it is desirable to use a chamber burette

[1] Amalgamated zinc is best prepared by dissolving 5 grams of mercury in 25 cc. of concentrated nitric acid with an equal volume of water, 250 cc. of water are added and the solution poured into 500 grams of shot zinc, 20-mesh. When thoroughly amalgamated the solution is poured off, and the zinc dried.

with graduations from 75 to 90 cc. in tenths and from 90 to 100 in twentieths of a cc. A titration of 90 to 100 cc. of the dichromate would require 0.9 to 1.1 gram of iron for a fifth normal solution and half this amount for a tenth normal solution of dichromate. In the first case 1.4 gram of Sibley iron ore should be taken and for N/10 0.7 gram of the ore. The ore is best dissolved in strong HCl, adding a few drops of stannous chloride solution and heating just below boiling. In case of an ore or iron ore briquette, containing silica in an appreciable amount, a carbonate fusion of the residue may be necessary. Reduction and titration of the ore is done exactly as prescribed under Procedure below.

The equivalent iron in the ore divided by the cc. titration required for complete oxidation gives the value in terms of grams per cc., e.g., 1.4 gram of ore containing 69.2% Fe required a titration of 95 cc. $K_2Cr_2O_7$ solution, then,

$$1 \text{ cc.} = \frac{(69.2 \times 1.4)}{100} \div 95 = 0.0102 \text{ gram Fe.}$$

Stannous Chloride. Sixty grams of the crystallized salt dissolved in 600 cc. of strong HCl and made up to one liter. The solution should be kept well stoppered.

Mercuric Chloride. Saturated solution of $HgCl_2$ (60 to 100 grams per liter).

Potassium Ferricyanide, $K_3Fe(CN)_6$. The salt should be free of ferrocyanide, as this produces a blue color with ferric salts, which would destroy the end-point. It is advisable to wash off the salt before using. A crystal the size of a pinhead dissolved in 50 cc. of water is sufficient for a series of determinations. The solution should be made up fresh for each set of determinations.

Apparatus. ***Chamber burette.*** This should read from 75 to 90 cc. in tenths and from 90 to 100 cc. in twentieths of a cc.

Test Plate. The usual porcelain test-plate with depressions may be replaced by a very simple and efficient test-sheet made by dipping a white sheet of paper in paraffin. The indicator does not cling to this surface, the drops assuming a spherical form, which renders the detection of the end-point more delicate.

Procedure. Iron Ores. The amount of sample taken should be such that the actual iron present would weigh between 0.9 to 1.1 gram. This weight can be estimated by dividing 95 by the approximate percentage of iron present, e.g., for 50% Fe ore take $\frac{95}{50} = 1.9$ gram; 95% iron material would require 1 gram, whereas 20% Fe ore would require 4.75 grams.

For samples containing less than 20% Fe it is advisable to use N/10 $K_2Cr_2O_7$ solution.

The sample should be finely ground (80-mesh).

Solution. The hydrochloric acid method for solution of the oxidized ore with subsequent carbonate fusion of the residue is recommended as being suitable for iron ores, briquettes, and materials high in iron.

Reduction. H_2S reduction is recommended in ores containing arsenic or titanium. $SnCl_2$ in very slight excess, followed by mercuric chloride, $HgCl_2$, gives excellent results in absence of other reducible salts of elements, Cu, As, etc.

Test Lead. The easy manipulation and efficiency of this method of reduction makes it applicable for a large variety of conditions. The acid solution preferably, HCl, is diluted to about 150 to 200 cc., containing 15 to 20 cc. concentrated hydrochloric acid (sp.gr. 1.19). Sufficient test lead is added to cover the bottom of a No. 4 beaker. The solution covered is boiled vigorously until it becomes colorless. Copper, if present, is precipitated, as well as platinum,

and small amounts of arsenic and antimony eliminated from the solution during the reduction of the iron. The cooled solution is poured into a 600-cc. beaker and the mat of lead remaining in the No. 4 beaker washed free of iron, two or three 50-cc. washings being sufficient. The main solution and washings are combined for titration. If the solution is slightly colored, due to reoxidation of iron, a few drops of stannous chloride solution are added to reduce it, followed by an excess of $HgCl_2$ solution, 20 to 25 cc., and allowed to stand five minutes.

Titration. The standard potassium dichromate is run into the solution to within 5 to 10 cc. of the end-point, this having been ascertained on a portion of the sample. The dichromate is run in slowly near the end-reaction, and finally drop by drop until a drop of the solution mixed with a drop of potassium ferricyanide solution produces no blue color during thirty seconds. A paraffined surface is excellent for this test.

Cc. $K_2Cr_2O_7$ multiplied by value per cc. = Fe present in sample. $\% = \frac{\text{Fe} \times 100}{\text{wt. taken}}$.

NOTES. If $SnCl_2$ solution has been used for reduction of the iron, it is necessary to add the $HgCl_2$ rapidly to a cold solution, as slow addition to a warm solution is apt to precipitate metallic mercury.

In case an excess of dichromate has been added in the titration, as often occurs, back titration may be made with ferrous ammonium sulphate $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$. N/10 solution of this reagent may be prepared by dissolving 9.81 grams of the clear crystals in about 100 cc. of water, adding 5 cc. of concentrated H_2SO_4 and making to 250 cc. The solution should be standardized against the dichromate solution to get the equivalent values, by running the dichromate directly into the ferrous solution.

The ferricyanide indicator should be made up fresh each time it is required.

Large amounts of manganese in the iron solution titrated cause a brown coloration, which masks the end-point. Nickel and cobalt, present in large amounts, are objectionable for the same reason. This interference may be overcome by using very dilute acid solutions of ferricyanide indicator, so that the insoluble ferricyanide of these metals will not form.

Potassium Permanganate Method for Determination of Iron

Introduction. The method depends upon the quantitative oxidation of ferrous salts to the ferric condition when potassium permanganate is added to their cold solution, the following reaction taking place:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Hydrochloric acid in presence of iron salts has a secondary reaction upon the permanganate, e.g.,

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 10Cl.$$

This reaction may be prevented by addition of large amounts of zinc or manganous sulphates together with an excess of phosphoric acid.[1] It is preferable, however, to expel HCl, when this has been used as a solvent, by adding sulphuric acid and taking to fumes. The solution is diluted and reduced with zinc and titrated as directed.

The reduction of ferric sulphate is best accomplished by passing the solution through a column of amalgamated zinc in the Jones reductor. In presence of titanium, reduction is accomplished by H_2S in a hydrochloric acid solution of the iron.

[1] Jour. Am. Chem. Soc., **17**, 405.

Since potassium permanganate enters into reaction with acid solutions of antimony, tin, platinum, copper and mercury, when present in their lower state of oxidation, (also with manganese in neutral solutions) and with SO_2, H_2S, N_2O, ferrocyanides and with most soluble organic bodies, these must be absent from the iron solution titrated.

Potassium permanganate produces an intense pink color in solution, so that it acts as its own indicator.

Solutions Required. ***Standard Permanganate Solutions.*** As in case of potassium dichromate, it is convenient to have two standard solutions, N/5 and N/10.

From the reaction given above it is evident that 2 $KMnO_4$ are equivalent to 5 oxygens, e.g., $2KMnO_4 = K_2O + 2MnO + 5O$, hence a normal solution would contain one-fifth of the molecular weight of $KMnO_4 = 31.6$ grams of the pure salt. Hence a N/5 solution would contain 6.32 grams per liter and a N/10 solution 3.16 grams.

Since commercial potassium permanganate is seldom pure, it is necessary to determine its exact value by standardization. This is commonly accomplished by any of the following methods:

(*a*) By a standard electrolytic iron solution.

(*b*) By ferrous salt solution, e.g., $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.

(*c*) By oxalic acid or an oxalate.

Reaction. $2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O$.

Standardization of $KMnO_4$ against *sodium oxalate* is recommended as the most accurate procedure. The salt has no water of crystallization and is not hygroscopic. It can be obtained from the Bureau of Standards with a guarantee of purity. Traces of moisture can be expelled by heating the salt to 120° C. for two hours, then cooling in a desiccator.

N/5 $Na_2C_2O_4$ contains 13.40 grams per liter, N/10 solution contains 6.7 grams. For standardization of N/5 $KMnO_4$, 3.35 grams of the sodium oxalate are dissolved in warm (70° C.) water (about 200 cc.), 50 cc. of 2N. H_2SO_4 are added and the solution made up to 250 cc.

N/5 $KMnO_4$ contains 6.32 grams of the salt per liter. It is advisable to dissolve 6.4 grams of the salt in about 500 cc. of hot water and filter the solution through asbestos to remove any dioxide of manganese that may be present, as MnO_2 aids in the decomposition of $KMnO_4$ solution. The reagent should be kept tightly sealed in a dark bottle well protected from the light. This solution should stand two or three days before standardization.

To standardize the solution 100 cc. of the N/5 sodium oxalate solution is heated to about 70° C. and the permanganate solution added from a 100-cc. burette very slowly in small portions at a time, allowing the color to fade after each addition before adding more. When within 5–10 cc. of the end-point the permanganate solution should be added drop by drop until a faint permanent pink color persists.

Procedure for the Determination of Iron by the Jones Reductor

Preparation of Sample. Such an *amount* of the sample is taken that the iron content is between two- and three-tenths of a gram (0.2 to 0.3 gram). If hydrochloric acid has been required to effect solution, or hydrochloric acid and

nitric acid (25 cc. : 1 cc.), as in case of iron and steel, 4 to 5 cc. conc. sulphuric are added, and the solution evaporated to small bulk on the steam bath and to SO_3 fumes to remove hydrochloric acid. The iron is taken up with about 50 cc. dilute sulphuric acid, 1 : 4, heating if necessary, and filtering if an insoluble residue remains.

Preparation of the Reductor. Cleaning out the apparatus. See Fig. 40. The stop-cock of the reductor is closed, a heavy-walled flask or bottle is put into position at the bottom, and 50 cc. of dilute sulphuric acid poured into the funnel. The cock is opened and the acid allowed to flow slowly through the zinc in the tube, applying a gentle suction. Before the acid has drained out of the funnel, 50 cc. of water are added, followed by 50 cc. more of dilute sulphuric acid and 50 cc. of water in turn. The stop-cock is turned off before the water has drained completely from the funnel so that the zinc is always covered by a solution of acid or water. This precaution should be observed in all determinations with the Jones reductor to prevent the inflow of air into the column of zinc. The contents of the flask being emptied and the flask replaced, the apparatus is ready for the determination of the blank.

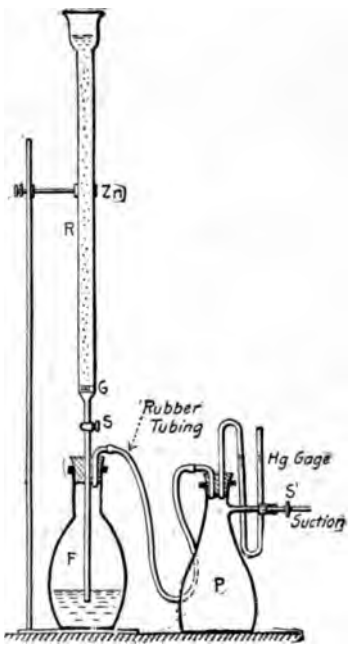


FIG. 40.—Jones Reductor.

Determination of the Blank. Fifty cc. of dilute sulphuric acid, 1 : 4, are passed through the reductor, followed by 250 cc. of distilled water, according to the directions given above. The acid solution in the flask is then titrated with N/10 $KMnO_4$ solution. If more than 3 or 4 drops of the permanganate are required, the operation must be repeated until the blank titration does not exceed this amount. The final blank obtained should be deducted from the regular determinations for iron. The end-point of the titration is a faint pink, persisting for one minute.

Reduction and Titration of the Iron Solution. The sample is diluted to 200 cc., and, when cold, is run into the funnel, the stop-cock opened and the solution drawn slowly through the column of zinc into the flask, about four minutes being required for 200 cc. of solution. Before the funnel has completely drained, rinsings of the vessel which contained the sample are added; two 50-cc. portions are sufficient, followed by about 50 cc. of water. The stop-cock is closed before the solutions have completely drained from the funnel.

Titration. The flask is removed and tenth normal solution of permanganate added until a faint pink color, persisting one minute, is obtained. The blank is deducted from the cc. reading of the burette.

Cc. $KMnO_4$ thus found multiplied by the value of the reagent in terms of N/10 = true value of N/10 $KMnO_4$ required to oxidize the reduced iron.

One cc. N/10 $KMnO_4$ = .005584 gram Fe; or .007984 gram Fe_2O_3.

This weight, divided by the weight of the sample taken, and multiplied by 100 = per cent iron, or iron oxide in the sample, according to the factor taken above.

Stannous Chloride Method for Determination of Ferric Iron

The procedure is based upon the reduction of the yellow ferric chloride to the colorless ferrous salt by stannous chloride, the following reaction taking place:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The method is of value in estimating the quantity of ferric iron in presence of ferrous, where the two forms are to be determined. In order to obtain the total iron the ferrous is oxidized by adding a few crystals of potassium chlorate and taking to dryness to expel chlorine, and then titrated with stannous chloride.

The accuracy of the method depends upon the uniformity of conditions of temperature, concentration, etc., of making the run with the sample and of standardizing the stannous chloride. The solution should be free from other oxidizing agents, or from salts that give colored solutions.

The amount of iron in terms of ferric oxide that can be estimated by this procedure ranges from 0.002 gram to 0.05 gram.

Reagents. ***Stannous Chloride Solution.*** The reagent is prepared by dissolving 2 grams of stannous chloride crystals in hot concentrated hydrochloric acid and making up to 1 liter. The solution should be kept in a dark bottle to which the titrating burette is attached in such a way that the liquid may be siphoned out into this, as shown in the illustration, Fig. 41. The air entering the bottle passes through phosphorus or pyrogallic acid to remove the oxygen. In this way, protected from the air, the reagent will keep nearly constant for several weeks. It is advisable, however, to restandardize the solution about every ten to fifteen days. One cc. will be equivalent to about 0.001 gram Fe.

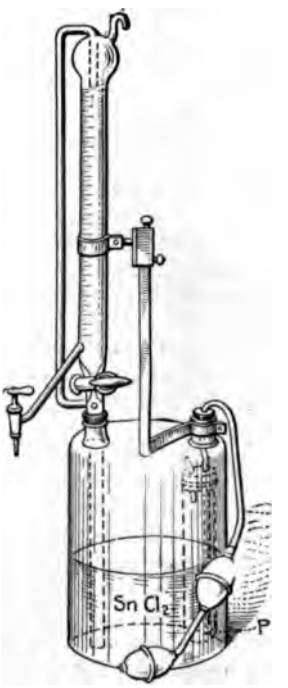


FIG. 41.—Apparatus for Stannous Chloride Titration of Iron.

Standard Iron Solution. 8.6322 grams of ferric ammonia alum is dissolved in dilute hydrochloric acid and made up to one liter. The iron is determined in 100-cc. portions by the dichromate method. One cc. will contain about 0.001 gram Fe.

Procedure. To the sample in a casserole is added 25 cc. of concentrated hydrochloric acid and an equal volume of water. The resulting solution is heated to boiling and quickly titrated with the stannous chloride reagent, until the yellow color fades out and the solution becomes colorless.

NOTE. The titration should be done quickly, as the iron will reoxidize on standing and the solution again become yellow. The true end-point is the first change to a colorless solution.

COLORIMETRIC METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF IRON

Iron Traces. Sulphocyanate (Thiocyanate) Method[1]

Introduction. By this method 1 part of iron may be detected in 50 million parts of water. The presence of free mineral acid increases the sensitiveness of the method, so that it is especially applicable to the determination of small amounts of iron in mineral acids. It is available in presence of many of the ordinary metals and in presence of organic matter. Silver, copper, cobalt, mercuric chloride, however, interfere.

Nitric acid gives a color with sulphocyanates that may be mistaken for iron.

This method, like the stannous chloride method, determines only the ferric iron. It is based on the fact that ferric iron and an alkali sulphocyanate, ammonium or potassium sulphocyanates, in an acid solution gives a red color, the intensity of which is proportional to the quantity of iron present. The color is due to the formation of the compound, $Fe(CNS)_3 \cdot 9KCNS \cdot 4H_2O$.

Reagents Required. ***Standard Iron Solution.*** A ferric solution, the iron content of which has been determined, is diluted and divided so as to obtain 0.0004 gram Fe. This is made up to 2 liters with water containing 200 cc. of iron-free, C.P. H_2SO_4. One hundred cc. of this solution, together with 10 cc. of normal ammonium sulphocyanate solution, is used as a standard. One hundred cc. contains 0.00002 gram Fe.

Normal sulphocyanate contains 76.1 grams of NH_4CNS per liter.

Procedure. The weighed sample, 1 to 10 grams, or more if necessary, is dissolved in dilute H_2SO_4 and oxidized by adding dilute permanganate, $KMnO_4$, solution drop by drop until a faint pink color is obtained. The sample is diluted to exactly 100 cc. and is poured into a burette graduated to $\frac{1}{10}$ cc. Two colorless glass cylinders of the 100-cc., Nessler type are used for comparison of standard and sample. Into one cylinder is poured 100 cc. of the standard solution, made as directed above. Into the second cylinder containing 10 cc. of sulphuric acid with 10 cc. ammonium sulphocyanate, NH_4CNS, diluted to 60 or 70 cc., the sample is run from the burette until the depth of the color thus produced on dilution to 100 cc. exactly matches the standard. From the number of cc. used the weight of the sample is calculated. One hundred cc. of the standard contains 0.00002 gram Fe.

Dividing the weight of iron in the standard by the weight of sample used and multiplying by 100 gives the per cent of iron in the sample.

NOTES. If other metals are present, that form two series of salts, they must be in the higher state of oxidation, or the color is destroyed. (Sutton.) Oxalic acid, if present, destroys the color. Oxidation with $KMnO_4$ or $KClO_3$ with subsequent removal of Cl_2 prevents this interference. (Lunge, C. N., **73**, 250.)

Chlorides of the alkaline earths retard or prevent the sulphocyanate reaction. (Weber, C. N., **47**, 165.)

The colorimeter used for the determination of minute quantities of lead would serve admirably for the determination of traces of iron by the sulphocyanate method.

Acids, hydrochloric or sulphuric (diluted), may be added directly to the ammonium sulphocyanate solution.

[1] Thomson, J. C. S., 493, 1885, and C. N., **51**, 259. Kruss and Moraht, C. N., **64**, 255. Davies, C. N., **8**, 163.

Salicylic Acid Method for Determining Small Amounts of Iron

Salicylic acid produces an amethyst color with neutral solutions of ferric salts, the depth of the color being proportional to the concentration of the ferric iron in the solution. The reaction is useful in determining small amounts of iron in neutral salts, such as sodium, ammonium, or potassium alums, sulphates, or chlorides, zinc chloride, etc. Phosphates, fluorides, thiosulphates, sulphites, bisulphites and free mineral acids should be absent. The sample should not contain over 0.0002 gram iron, as the depth of color will then be too deep for colorimetric comparisons. As low as 0.00001 gram ferric iron may be detected. Ferrous iron produces no color with the reagents, hence the procedure serves for determining ferric iron in presence of ferrous.

The material is dissolved in 20 cc. of pure water, the sample filtered if cloudy, and transferred to a Nessler tube. Dilute potassium permanganate solution is added until a faint pink color is produced and then 5 cc. of a saturated solution of salicylic acid. (The reagent is filtered and the clear solution used.) Comparison is made with standard solutions containing known amounts of ferric iron, the standards containing the same reagents as the sample. If desired the standard iron solution (0.086 gram ferric ammonium alum, clear crystals, dissolved in water containing 2 cc. of dilute sulphuric acid and made to 1000 cc., each cc. contains approximately 0.00001 gram Fe‴) is added from a burette to 5 cc. of salicylic acid diluted to 25 cc. in a Nessler tube, until the color of the standard matches the sample. A plunger is used to stir the liquids.

TECHNICAL ANALYSIS OF IRON AND STEEL

The elements carbon, manganese, phosphorus, sulphur, and silicon are invariable constituents of iron and steel, and are always included in an analysis. Copper and arsenic are sometimes found; aluminum, chromium, nickel, molybdenum, tin, titanium, tungsten, vanadium, and zinc occur in special alloy steels. Minute traces of oxygen, hydrogen, and of many other elementary constituents frequently are present, but are of so little importance that they are seldom considered in an analysis.

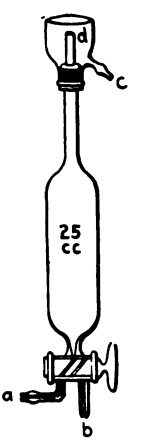


FIG. 42.
Dividing Pipette.

Our attention is drawn in this chapter to the more important constituents, whose estimation is required in the daily routine analysis of a steel works laboratory. The elements considered are carbon—carbide or combined carbon and graphitic carbon, manganese, phosphorus, sulphur, and silicon. Determination of the elements of special alloy steels containing aluminum, chromium, nickel, titanium, tungsten, vanadium, etc., are given in the chapters on the elements in question; for example the determination of vanadium in steel will be found in the chapter on Vanadium, chromium and copper in the chapters on Chromium and Copper, etc.

As is generally the case, a large number of determinations are required in the steel works laboratories and it is not an uncommon thing for one man to turn out 50 to 100 determinations a day. To accomplish this, simple and rapid procedures are required. When the metal is unusually high in an undesirable constituent it is indicated

by the test, and a confirmation of the result is obtained by an additional test exercising extreme care, and using a procedure giving results of the highest accuracy. Fortunately the analysis of steel has received considerable attention and rapid methods have been worked out which are extremely accurate.

The procedures briefly outlined have proven of value to analysts of iron and steel. While in charge of the laboratory at Baldwin Locomotive Works, the author found that a skilled analyst was able to turn out 125 determinations of combined carbon, or 100 of manganese, or of sulphur, or 50 determinations of phosphorus, or 25 determinations of silicon per day by the procedures given. This necessitates the use of a large number of beakers and flasks, ample desk room, individual balances, hot plates, and hoods to accommodate a dozen to two dozen beakers or flasks at a time, and a carefully planned system.

The dividing pipette, shown in Fig. 42, is useful for adding a definite amount of reagent to the sample.

In addition to the short methods, we include the procedures recommended by the U. S. Bureau of Standards, for cases where accuracy is essential and time a secondary consideration.

Preparation of the Sample

The metal is sampled by drilling with a clean twist drill, using no water or oil.

Hard grades of pig iron, chilled iron, ferromanganese, quenched steel, etc., are broken down to a coarse powder in a chilled steel mortar.

Combined or Carbide Carbon—Colorimetric Method

Rapid Method. 0.2 gram of well-mixed drillings is placed in a test-tube $6 \times \frac{3}{4}$ ins. and 4 to 10 cc. of nitric acid (sp.gr. 1.2) added from a burette, the test-tube being placed in cold water to prevent too violent action. The amount of acid added is governed by the carbon-content of the steel (see chapter on Carbon, page 108). After the violent action has ceased, the tube is placed in a specially-designed water bath, the water heated to boiling and boiled for twenty minutes or more until the solution in the tube has become perfectly clear. The sample is now removed, washed into a color carbon tube and compared with a standard steel of the same class of material as that examined. Full details of the procedure may be found in the chapter on Carbon.

Iron and steel containing graphite must be filtered before making comparisons. The solution, diluted with one-half its volume of water, is filtered through a small filter paper into a test-tube. The residue is washed with a fine jet of distilled water until free of color. The filtrate is compared with a standard sample of similar composition treated in the same way.

Steel containing chromium, copper, nickel, and elements yielding a colored solution should not be examined by the colorimetric methods.

Method of the Bureau of Standards. Total and graphitic carbon are determined and the difference taken as combined carbon.

Specifications for Combined Carbon.

Material.	Per cent Carbon.
Boiler rivets	0.15
Seamless boiler tubes	0.18–0.25
Boiler and fire-box plates	0.15–0.25
Cylinder grade pig iron	0.25–0.50
Forged and rolled steel wheels	0.70–0.75
Steel blooms for forgings, open hearth, basic	0.40 0.55
Steel blooms for forgings, acid	0.35–0.40
Bolt steel	0.22–0.28
Spring steel	0.90–1.10
Crank axles forged	0.35–0.55
Casting	not over 0.35
Tire steel	0.65–0.75
Floor grade pig iron	not over 0.40

Total Carbon

The determination is required for an accurate estimation of carbon where the color test indicates the carbon content outside the limits of requirement, or in cases where interfering substances are present. In material where the carbon content is of extreme importance, the color method is not used. Details of the procedure for determining carbon by direct combustion are given in the chapter on Carbon. The following procedure is recommended by the Bureau of Standards:

(*a*) **In Irons.** Two grams of iron are mixed with about twice the weight of purified ferric oxide. The mixture is placed in a platinum boat, which is lined with a suitable bed material, and is burned in a current of oxygen, as described below.

(*b*) **In Steels.** The method is the same as for irons with omission of the ferric oxide mixture.

Details of Direct Combustion Method. ***Furnaces and Temperature of Burning.*** Porcelain tubes wound with "nichrome" wire, provided with suitable heat insulation and electrically heated, are used, and readily give temperatures to 1100° C. Type FB 301 Hoskins tube furnace and the hinged type, Fig. 32*b*, are satisfactory. The temperature control is by means of an ammeter and rheostat in series with the furnace, with occasional check by a thermocouple.

Boats and Lining. Platinum boats provided with a long platinum wire for manipulation in the tube are mostly used; alundum ones occasionally. The bed or lining on which the steel rests is 90-mesh "RR alundum, alkali-free, specially prepared for carbon determination." A layer of this alundum is also placed in the bottom of the combustion tube to prevent the boat sticking to the glaze. A platinum cover for the boat is sometimes used, and is essential when the combustion is forced.

The nature and quality of the bed material are matters of great importance. Alumina as prepared from the sulphate or from alum may not be free from sulphate or alkali, both of which have given serious trouble at the Bureau. The alkali, if present, may not manifest itself by an alkaline reaction until after one or two combustions have been made, using the same bed material. Even the ordinary white "alundum" on the market carries a few hundredths of 1% of alkali. Iron oxide has been tried, and when pure should, apparently, give good

service. As yet, however, it has been difficult to obtain or prepare acceptable material for use with steels. Quartz sand gives rise to a fusible slag, which melting before combustion is complete, incloses bubbles of carbon dioxide gas. This defect would probably inhere in any other material of an acid character. The presence in the silica bed after combustion of crystals which appear to be carborundum, have occasionally been noted.[1]

Purity of Oxygen. Blanks. The Bureau makes its oxygen electrolytically, and its content of this element is usually 99 to 99.5%, and sometimes higher. Even with this gas a slight blank is usually obtained. When running a blank, in additional to the usual precautions, the rate at which the oxygen is introduced should be the same as when burning a sample, and the time should be three to five times as long.

Method of Admitting Oxygen and Rate of Combustion. The furnace being at the proper temperature, the boat containing the sample is introduced. Oxygen is admitted either at once or after the boat has reached the temperature of the furnace, as the operator prefers, or as the nature of the steel may demand. The rate of flow of the oxygen varies with the absorption apparatus used and with the preference of the operator, and may be considerably more rapid when absorbing carbon dioxide in soda lime than in an alkaline solution. A rapid flow of oxygen also facilitates the burning of resistant samples. A continuous forward movement of the gas current is maintained at all times. The time for a determination varies, of necessity, with the nature of the sample and the rate of flow of the oxygen, ranging from ten to thirty minutes. The endeavor is to obtain a well-fused oxide. With all samples close packing in a small space is conducive to rapid combustion and to fusion of the resulting oxide.

Authorities differ as to the advisability of allowing the oxide of iron to fuse thoroughly. Even when fusion does take place additional carbon dioxide is obtained very frequently by grinding the oxide and reburning. Often more than one regrinding and reburning is necessary in order to reduce the amount of carbon dioxide obtained to that of the constant blank.

Oxides of sulphur have been found very difficult to eliminate from the gases leaving the tube. Lead peroxide ("nach Dennstedt") heated to 300° C. and zinc at room temperature appear to retain them best.

Attention is called to the inadmissibility of using dry agents of different absorptive power in the same train, in positions where a difference could possibly affect results.

Weighing of Tubes. There is much greater difficulty in securing constant conditions when weighing absorption tubes than is usually considered to be the case. Electrical effects, caused by wiping as a preliminary to weighing, may occasionally cause errors in weight running into the milligrams. The use of counterpoises of equal volume and similar material and shape is recommended.

If tubes are weighed full of oxygen, care is necessary to secure a uniform atmosphere in them. Even though the attempt is made to keep the apparatus always full of oxygen, some air is admitted when the boat is pushed into the combustion tube, and a much longer time is required to displace this than is usually allowed, unless the flow of oxygen during aspiration is rapid. The same is true if the tubes are weighed full of air by displacing the oxygen left in them after the steel is burned. Another source of error may arise from the

[1] Statement of Mr. George M. Berry, of the Halcomb Steel Co.

air admitted when putting the boat into the tube, if this air contains much carbon dioxide, as is the case when a gas furnace is used. The boat is usually pushed at once into the hot furnace, and as combustion begins almost immediately, there is no opportunity for displacing this air before the steel begins to burn.

Graphite in Iron

Two grams of iron are dissolved in nitric acid (sp.gr. 1.20), using 35 cc. and heating very gently. The residue is collected on an asbestos felt, washed with hot water, then with a hot solution of potassium hydroxide (sp.gr. 1.10), followed by dilute hydrochloric acid and finally by hot water. After drying at 100° C., the graphite is burned in the same manner as the total carbon, but without admixture of ferric oxide.

Manganese in Iron and Steel. Ammonium Persulphate Method

Small amounts of manganese may be determined colorimetrically by the persulphate method, provided the sample does not contain over 1.5% of manganese. The procedure given in detail in the chapter on Manganese, page 267, in brief is as follows:

Reaction. $2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O = 5(NH_4)_2SO_4+5H_2SO_4+4HNO_3+2HMnO_4.$

0.1 to 0.2 gram of steel, according to the amount of manganese in the sample, is placed in a 10-in. test-tube and 10 cc. of nitric acid (sp.gr. 1.2) are added. The sample is heated in a water bath until the nitrous fumes are driven off and the steel is completely in solution. Fifteen cc. of silver nitrate solution are added to the cooled sample, followed immediately with about 1 gram of ammonium persulphate crystals. The solution is warmed (80 to 90° C.) until the color commences to develop, and then for half a minute longer, and then placed in a beaker of cold water until the solution is cold. Comparison is now made with a standard steel treated in the same way. The comparison being made exactly as indicated for determining carbon by the color method. See chapter on Carbon.

Example. If the standard, containing 0.6% Mn is diluted to 15 cc., each cc. = 0.04% Mn. If the sample required a dilution of 20 cc. to match the standard, then $0.04\times20=0.8\%$ Mn.

Lead Oxide Method (Deshey).

Oxidation of the manganese in the steel is effected in a nitric acid solution by addition of red lead (or by lead peroxide); the lead peroxide, formed oxidizes the manganese nitrate to permanganic acid. The solution is now titrated with standard sodium arsenite, the following reaction taking place:

$$2HMnO_4+5Na_3AsO_3+4HNO_3=5Na_3AsO_4+3H_2O+2Mn(NO_3)_2.$$

0.5 gram of steel is placed in a 150-cc. beaker and dissolved with about 30 cc. of nitric acid (sp.gr. 1.12). After violent action has subsided, the beaker

is placed on a hot plate and when the iron has dissolved, 20 cc. of water added. The manganese is now oxidized by adding red lead in small portions at a time, until the solution appears brown with a pinkish purple foam on the surface. The solution is diluted with hot water until the volume is about 100 cc. and then boiled for a few minutes. It is now placed in a dark closet to cool. (A fresh batch of samples may be started in the meantime.) The solution is carefully decanted off from the peroxide, and with the washings of the peroxide residue, titrated with standard sodium arsenite to the yellowish green end-point. The sodium arsenite is made by dissolving 4.96 grams of pure arsenous acid together with 25 grams of sodium carbonate in 200 cc. of hot water and the solution diluted to 2500 cc. The arsenite is standardized against a steel sample of known manganese content, or against standard permanganate solution.

Bismuthate Method for Determining Manganese, Recommended by the U. S. Bureau of Standards[1]

This is the most accurate method for determining manganese in iron and steel. The procedure is as follows:

Procedure. One gram of drillings is dissolved in 50 cc. of nitric acid (sp.gr. 1.135) in a 200-cc. Erlenmeyer flask. Irons should be filtered. The solution is cooled, about 0.5 gram of sodium bismuthate is added, and it is then heated until the pink color has disappeared. Any manganese dioxide separating is dissolved in a slight excess of a solution of ferrous sulphate or sodium sulphite. The solution is boiled till free from nitrous fumes. After cooling to 15° C., a slight excess of bismuthate is added and the flask is shaken vigorously for a few minutes. Then 50 cc. of 3% nitric acid is added and the solution is filtered through asbestos. A measured excess of ferrous sulphate is run in and the excess titrated against permanganate solution which has been compared with the iron solution on the same day. A great many steels now carry small amounts of chromium as impurity. In such cases titration against arsenite solution is recommended, or removal of the chromium by zinc oxide and subsequent determination of the manganese by the bismuthate method.

Permanganate solutions are standardized against sodium oxalate (Bur. Stds. Sample No. 40) as prescribed by McBride.[2]

Specifications for Manganese in Iron and Steel

Material.	Percentage of Manganese.
Boiler rivets	0.30–0.60
Boiler and fire-box plates	not over 0.45
Seamless boiler tubes	0.40–0.65
Floor-grade pig iron	not over 0.80
Cylinder-grade pig iron	0.50–0.80
Forged and rolled steel wheels	0.60–0.80
Steel blooms for forgings	not over 0.70
Bolt steel	not under 0.50
Spring steel	not over 0.50 (0.25 desired)
Crank axles, forged	not over 0.75
Castings	not over 0.75
Tire steel	0.50–0.75

[1] See page 263.

[2] Bull. Bur. Sds., 8, 641. J. Am. Chem. Soc., **34**, 393, 1912.

Determination of Phosphorus

The procedures outlined by the Bureau of Standards are generally used in steel works laboratories.

(*a*) **Preparation of Solution and Precipitation of Phosphorus.** Two grams of sample are dissolved in nitric acid (sp.gr. 1.135) and the solution is boiled until brown fumes no longer come off. Ten cc. of permanganate solution (15 grams to 1 liter) are added, and the boiling is continued. Sodium sulphite solution is added to dissolve the oxide of manganese, and the solution is again boiled and then filtered. With irons the insoluble residue should be tested for phosphorus. After cooling the filtrate, 40 cc. of ammonia (sp.gr. 0.96) are added, the solution is agitated, and when the temperature is at 40° C., 40 cc. of molybdate solution [1] are added and the solution is shaken vigorously for five minutes. After settling out, the yellow precipitate is treated according to one of the following methods, *b* or *c*:

(*b*) **Alkalimetric Method.** The precipitate is washed with 1% nitric acid solution followed by 0.1% potassium nitrate solution until the washings are no longer acid. The precipitate is dissolved in a measured excess of standardized sodium hydroxide solution and titrated back with standardized nitric acid using phenolphthalein. The solutions are standardized against a steel with a known amount of phosphorus.

(*c*) **Molybdate Reduction Method.** The precipitate is washed ten to fifteen times with acid ammonium sulphate (prepared according to Blair) or until the washings no longer react for iron or molybdenum. It is dissolved in 25 cc. of ammonia (5 cc. ammonia of 0.90 sp.gr. to 20 cc. water). The filter is washed well with water and 10 cc. of strong sulphuric acid added to the filtrate, which is run through the reductor at once and titrated against a N/30 permanganate solution which has been standardized against sodium oxalate, as prescribed by McBride.[2]

Specifications for the Amount of Phosphorus

Class of Material.	Limit of Phosphorus Allowed, per cent.
Boiler steel	0.05
Forged and rolled steel wheels	0.05
Steel blooms for forgings	0.05
Crank axles	0.05
Tire and bolt steel	0.05
Spring steel	0.05
Spring steel desired	0.03
Fire-box plates	0.03
Castings	0.06
Floor-grade pig iron	0.5–0.9
Cylinder iron	0.5–0.9

Determination of Sulphur

Rapid-evolution Method. Volumetric. Five grams of iron or steel are placed in a 500-cc. Erlenmeyer flask, provided with a two-holed rubber stopper, through which passes a long-stem thistle tube reaching to the bottom of the

[1] Blair, "Chemical Analysis of Iron," (7th Ed.), p. 97.
[2] Bull. Bur. Stds., 8, 641. J. Am. Chem. Soc., 34, 393, 1912.

flask, and a delivery-bulb condenser, connected by means of a rubber tube to an absorption bulb. (See sketch of apparatus in the chapter on Sulphur, volumetric methods, page 399.)

About 25 to 35 cc. of an ammoniacal solution of cadmium chloride are placed in the absorption bulb, the apparatus connected and about 100 cc. of dilute hydrochloric acid (sp.gr. 1.1) poured through the thistle tube into the flask containing the drillings. The mixture is heated gently until the sample goes into solution and then boiled until steam escapes from the apparatus. The reagent in the absorption bulb should remain alkaline, otherwise a loss of sulphur is apt to occur.

The absorption bulb is now disconnected and the contents emptied into a 400-cc. beaker and the bulb washed out with dilute hydrochloric acid after first rinsing out once or twice with water. The solution is now diluted to about 300 cc., and if not already acid, is made so by addition of more hydrochloric acid.

Two to 3 cc. of starch indicator are added and the mixture titrated with standard iodine, stirring constantly during the titration. A permanent blue color in the end-point sought. If much cadmium sulphide is present additional hydrochloric acid may be required.

The number of cc. of iodine solution required multiplied by the factor of iodine to sulphur gives the amount of sulphur present in the sample taken.

NOTES. For a more complete description of the procedure see chapter on Sulphur. With certain pig irons low results are apt to be obtained by the evolution method. For such the gravimetric method given is recommended.

Gray iron will evolve all its sulphur as H_2S, white iron, gray water-chilled iron, gives up only part of its sulphur by the evolution method. The method gives low results for high carbon steel.

In place of absorbing the H_2S in cadmium chloride, the Bureau of Standards recommends absorption in an ammonicaal solution of hydrogen peroxide (5 cc. H_2O_2 3%+25 cc. NH_4OH, sp.gr., 0.90). The sulphuric acid formed is precipitated from a slightly hydrochloric acid solution, by barium chloride and weighed as $BaSO_4$.

Method by the U. S. Bureau of Standards. Gravimetric Sulphur by Oxidation

Five grams of iron or steel are dissolved in a 400-cc. Erlenmeyer flask, using 50 cc. of strong nitric acid. A little sodium carbonate is added, the solution is evaporated to dryness, and the residue baked for an hour on the hot plate. To the flask 30 cc. of strong hydrochloric acid are added, and the evaporation and baking are repeated. After solution of the iron in another 30 cc. of strong hydrochloric acid and evaporation to a sirupy consistency, 2 to 4 cc. of the same acid are added, followed by 30 to 40 cc. of hot water. The solution is then filtered and the residue washed with hot water. The sulphur is precipitated in the cold filtrate (about 100 cc.) with 10 cc. of a 10% solution of barium chloride. After forty-eight hours the precipitate is collected on a paper filter, washed first with hot water (containing 10 cc. of concentrated hydrochloric acid and 1 gram of barium chloride to the liter) until free from iron and then with hot water till free from chloride; or, first with cold water, then with 25 cc. of water containing 2 cc. of concentrated hydrochloric acid to the liter. The

washings are kept separate from the main filtrate and are evaporated to recover dissolved barium sulphate.

With irons the paper containing the insoluble residue above mentioned is put into a platinum crucible, covered with sodium carbonate free from sulphur, and charred without allowing the carbonate to melt. The crucible should be covered during this operation. Sodium nitrate is then mixed in and the mass fused with the cover off. An alcohol flame is used throughout. The melt is dissolved in water and evaporated with hydrochloric acid in excess to dryness in porcelain. The evaporation with water and hydrochloric acid is repeated to insure removal of nitrates. The residue is extracted with a few drops of hydrochloric acid and water, the insoluble matter is filtered off, and barium chloride is added to the filtrate. The barium sulphate obtained is added to the main portion.

Careful blanks are run with all reagents.

Specifications for Sulphur in Iron and Steel

Material.	Specifications, per cent.
Seamless boiler tubes..... must be below	0.05
Cylinder iron.....	0.05
Forged and rolled steel wheels.....	0.05
Steel blooms for forgings, basic and acid open hearth.....	0.05
Bolt steel.....	0.05
Spring steel.....	0.05
Crank axles.....	0.05
Tire steel.....	0.05
Castings.....	0.06
Boiler rivets.....	0.04
Floor-grade iron.....	0.04
Boiler plates.....	0.035
Fire-box plates.....	0.035
Amount desired in spring steel.....	0.030
Muck bar iron.....	0.02

Determination of Silicon

One gram of pig iron, cast iron, and high silicon iron, or 5 grams of steel, wrought iron, and low silicon iron are taken for analysis. (By taking multiples of the factor weight 0.4693, SiO_2 to Si, the final calculation is simplified.) The sample is placed in a 250-cc. beaker and 20 to 50 cc. of dilute nitric acid added. If the action is violent, cooling the beaker in water is advisable. When the reaction subsides, 20 cc. of dilute sulphuric acid, 1 : 1, are added, the mixture placed on the hot plate and evaporated to dense white fumes. The residue is taken up with 150 cc. of water containing 2 to 5 cc. of sulphuric acid and heated until the iron completely dissolves.

The solution is filtered and the silica residue washed first with hot dilute hydrochloric acid, sp.gr. 1.1, and then with hot water added in small portions to remove the iron sulphate. The residue is now ignited and weighed as silica.

NOTE. If the ash is colored by iron oxide, silica is determined by difference, after expelling the silica by adding 4 to 5 cc. of hydrofluoric acid and a few drops of sulphuric, taking to dryness and igniting the residue.

The following acid mixtures are recommended by the U. P. Ry. For steel, wrought iron and low silicon iron, 8 parts by volume of HNO_3, sp.gr. 1.42; 4 parts of conc. H_2SO_4, sp.gr. 1.84; 6 parts HCl, sp.gr. 1.2 and 15 parts by volume of water. For

dissolving pig iron, cast iron and high silicon iron, a mixture of 8 parts by volume of strong nitric acid and 5 parts of strong sulphuric acid, diluted with 17 volumes of water is used.

Rapid Method for Determining Silicon in Foundry Work. Liquid iron, dropped into cold water from a ladle 3 ft. above the water, will form shot shaped according to forms resulting from its chemical constitution, silicon being an important factor. Round shot, concave upper surface, $\frac{1}{4}$ to $\frac{3}{8}$ in. in diameter, indicate over 2% silicon. Flat, or irregular shot indicate low silicon. Shot with elongated tails indicate very low silicon.

Method of the U. S. Bureau of Standards for Silicon

The insoluble residue obtained in preparing the iron or steel for the gravimetric sulphur determination is filtered off, ignited in platinum, and weighed. Evaporation with a little hydrofluoric acid and 1 drop of sulphuric acid and subsequent ignition gives by the loss of weight silica corresponding to the silicon of the sample.

Specifications for Silicon in Iron and Steel

Material.	Amount of Silicon, per cent.
Boiler and fire-box plates	not over 0.03
Floor-grade pig iron	2.25–2.75
Cylinder-grade pig iron	1.25–1.60
Forged and rolled steel wheels	not over 0.20
Spring steel	not over 0.25 (0.15 desired)
Tire steel	under 0.25

LEAD

WILFRED W. SCOTT

Pb, *at.wt.* 207.2; *sp.gr.* 11.34; *m.p.* 327°; *b.p.* 1525° C; *oxides*, PbO, PbO_2, Pb_3O_4.

DETECTION

Hydrochloric acid precipitates lead incompletely from its cold solution as white $PbCl_2$, soluble in hot water by which means it is separated from mercurous chloride and silver chloride. $PbCl_2$ forms needle-like crystals upon cooling the extract.

Hydrogen sulphide precipitates black PbS from slightly acid solutions along with the other elements of the group.[1] Yellow ammonium sulphide, sodium sulphide and the fixed alkalies dissolve out arsenic, antimony and tin. The sulphide of lead, together with bismuth, copper and cadmium, dissolve in hot dilute nitric acid, leaving mercuric sulphide insoluble. The extract evaporated to dryness and then to SO_3 fumes, after addition of sulphuric acid, expels nitric acid. Upon adding water to the residue and boiling with a little additional sulphuric acid the sulphates of bismuth, copper and cadmium are dissolved out, lead sulphate remaining as a white residue.

Lead may be further confirmed by dissolving the sulphate in ammonium acetate (barium sulphate is very slightly soluble,) and precipitating the yellow chromate, $PbCrO_4$, by addition of potassium dichromate solution.

ESTIMATION

The determination of lead is required in valuation of its ores—galena, PbS; anglesite $PbSO_4$; cerussite, $PbCO_3$; krokoite, $PbCrO_4$; pyromorphite, $3Pb_3P_2O_8 \cdot PbCl_2$. It is determined in lead mattes; certain slags; drosses from hard lead; cupel bottoms; skimmings; lead insecticides (arsenate of lead); paint pigments such as white lead, red lead, yellow and red chromates, etc. It is determined in alloys such as solder, type metal, bell metal, etc. The estimation is necessary in the complete analysis of a large number of ores, especially in minerals of antimony and arsenic. Traces of lead are determined in certain food products where its presence is undesirable.

Preparation and Solution of the Sample

In dissolving lead, its alloys, or ores the following facts will be recalled. Hot, dilute nitric acid is the best solvent of the metal. Lead nitrate is insol-

[1] Lead precipitates best from solutions containing 1 cc. of concentrated free hydrochloric acid (sp.gr. 1.19) for each 100 cc. of solution. The sulphide is appreciably soluble if the acidity is increased to 3 cc. HCl per 100 of solution.

uble in concentrated nitric acid, but dissolves readily upon dilution with water. The metal is insoluble in dilute sulphuric acid, but dissolves in the hot, concentrated acid. Although not soluble in dilute hydrochloric, it dissolves in the hot, concentrated acid, especially in presence of the halogens chlorine, bromine and iodine. The metal is soluble in glacial acetic acid. The salts are soluble in hot, dilute nitric acid. In dissolving sulphide ores it should be kept in mind that strong nitric acid will form some lead sulphate which will be precipitated upon dilution of the solution. Oxidation is less apt to occur with the dilute acid. Silicates and slags require fusion with sodium carbonate and potassium carbonate. The cooled mass may then be extracted with hot water to remove silica and the residue containing the carbonates of the heavy metals dissolved in dilute nitric acid. Lead salts are soluble in ammonium acetate.

Ores, Minerals of Lead, etc. One gram of ore if rich in lead (galena), or more if the lead content is low, is placed in a platinum dish and 40 to 50 cc. of a mixture of one part concentrated sulphuric acid (sp.gr. 1.84) and three parts of concentrated nitric acid (sp.gr. 1.42) added. The covered dish is heated gently until the violent action has ceased, the cover is then rinsed off and 10 to 15 cc. of hydrofluoric acid, HF, added. The mixture is evaporated to SO_3 fumes (hood), but not to dryness, and cooled. The concentrate is diluted with 100 cc. of distilled water and digested on the steam bath until the salts are in solution. The insoluble lead sulphate is filtered and washed with 10% sulphuric acid solution and finally with 50% alcohol.

It may be advisable, in certain cases, to open up the ore with nitric acid or aqua regia, followed by sulphuric acid and hydrofluoric acid.

Iron Pyrites and Ores with Large Amounts of Impurities with Small Amounts of Lead. Ten grams of the sample or more, if lead is present in very small amounts (less than 0.1%), are taken for analysis, and 50 cc. of a mixture of potassium bromide and bromine solution added (75 grams of KBr dissolved in 400 cc. of water and 50 cc. of bromine added). After ten to fifteen minutes about 50 cc. of concentrated nitric acid are added and after the violent reaction has ceased 25 to 30 cc. of concentrated hydrochloric acid and the solution is evaporated on the hot plate to near dryness. Fifty cc. of C.P. (lead free) concentrated sulphuric acid is now added and the sample taken to fumes of SO_3 on a sand bath. After cooling, the concentrate is diluted to 500 cc. with water, about 5 cc. of strong sulphuric acid added, the solution heated to boiling and cooled. The precipitate is filtered by decantation onto a fine-grained filter (quality of an S. & S. 590 or B. & A. grade A), the residue boiled with more water containing H_2SO_4 and again decanted. This is repeated until all the iron sulphate is removed. (The filtrates should be kept several hours to see whether any of the lead has passed through the paper in a colloidal condition.) The precipitate is finally poured on the filter and washed with 2% H_2SO_4. Impure residues are extracted for lead with ammonium acetate.

Solution of Lead Alloys. As a rule these are best decomposed by treating 0.5 to 1.0 gram of the material, or more as the case may require, with a hot solution of nitric acid, 1 : 1, and evaporating the solution to low bulk, but not to dryness. Hot water is now added and the material boiled and the soluble portion filtered off. The insoluble material is digested with concentrated hydrochloric acid to which a little bromine has been added. Boiling the mixture will generally effect solution. (It must be remembered that lead chloride is difficultly soluble in cold dilute solutions.) The lead is converted to $PbSO_4$

by addition of sulphuric acid and taking to SO_3 fumes as in case of ores. The purification of the impure sulphate will be given later.

Lead may be precipitated as the chloride in the presence of a large excess of absolute alcohol and filtered free practically from impurities.

Brass and bronze may be dissolved in hot dilute nitric acid, 1 : 1. Bearing metal is best treated with a mixture of hydrochloric acid 5 parts and nitric acid 1 part.

SEPARATIONS

Separation of Lead as Sulphate. Lead is most frequently separated from other metals by precipitation as sulphate, $PbSO_4$, according to the details given under "Preparation and Solution of the Sample." In the presence of much bismuth or iron it is necessary to wash the precipitate with a 10% sulphuric acid solution to keep the bismuth in solution and to prevent the formation of the difficultly soluble basic ferric sulphate. In absence of appreciable amounts of these elements the lead sulphate is more completely separated by adding to the dilute sulphuric acid solution an equal volume of alcohol, filtering and washing the residue with 50% alcohol.

Separation of Lead from Barium. In the analysis of minerals containing barium, the insoluble sulphate, $BaSO_4$, will be precipitated with lead. Since barium sulphate is slightly soluble in ammonium acetate it will contaminate the lead in the subsequent extraction by this reagent. The presence, however, of a little sulphuric acid, renders this solubility practically negligible. The sulphuric acid should not exceed 1–2% in the ammonium acetate reagent, as lead sulphate will precipitate if sufficient sulphuric acid is added to the acetate extract. (Lead sulphate is precipitated almost completely if the acetate solution contains 10% sulphuric acid.)

Lead may be separated from barium sulphate by digesting the mixed sulphates with ammonium carbonate solution, whereby the lead sulphate is transposed to lead carbonate and ammonium sulphate, while barium sulphate is not changed. The soluble ammonium sulphate may be washed out with ammonium solution followed by water. Since lead carbonate is slightly soluble in the ammonium salt, the filtrate is treated with hydrogen sulphide and the dissolved lead recovered as PbS. The residue containing lead carbonate and barium sulphate is treated with dilute nitric or acetic acid. Lead passes into solution, while barium sulphate remains insoluble.

Extraction of Lead from the Impure Sulphate by Ammonium Acetate. The filter containing the impure sulphate, obtained by one of the procedures for solution of the sample, is placed in a casserole and extracted with about 50 cc. of hot, slightly ammoniacal ammonium acetate, the stronger the acetate the better. The clear liquid is decanted through a filter and the extraction repeated until the residue is free from lead (i.e., no test is obtained for lead with $K_2Cr_2O_7$). A very effective method of extraction is by adding solid ammonium acetate directly to the sample on a filter and pouring over it a hot solution of ammonium acetate. The filtrate containing the pure lead acetate solution may now be examined by one of the following procedures.

Lead sulphate containing arsenic should be dissolved in ammonium acetate, the extract made alkaline and lead precipitated as PbS. Arsenic remains in solution.

The isolation of minute quantities of lead from large amounts of other substances is described under "Gravimetric Methods for Traces of Lead."

GRAVIMETRIC METHODS

Determination of Lead as the Sulphate, $PbSO_4$

Procedure. The sample having been dissolved according to a method outlined, the lead precipitated as $PbSO_4$ by addition of an excess of sulphuric acid, and taking to SO_3 fumes, the lead sulphate is filtered off, upon cooling and diluting the sample. The $PbSO_4$ is washed with water containing 10% H_2SO_4 until free from soluble impurities. If insoluble sulphates or silica are present the lead must be purified. If such impurities are known to be absent (alloys), the sulphate may be filtered directly onto an asbestos mat in a tared Gooch crucible, dried, then ignited to dull red heat, cooled and finally weighed as $PbSO_4$. In the analysis of ores, however, it is generally advisable to purify the sulphate.

Purification of Lead Sulphate. Details of the procedure have been given under Separations—Extraction of Lead from the Impure Sulphate. The lead sulphate having been brought into solution by extraction with strong ammonium acetate solution, the excess acetic acid is volatilized by evaporation, the residue cooled and diluted with water. An excess of sulphuric acid is added and the precipitated sulphate is filtered off, washed with dilute sulphuric acid and alcohol, dried at about 110° C. and weighed.

$PbSO_4 \times 0.6831 = Pb$. Pb multiplied by 100 and divided by weight of sample taken equals per cent.

NOTES. Lead sulphate may be precipitated from ammonium acetate solution by adding sulphuric acid until the solution contains approximately 10% H_2SO_4.

An acetate extraction may not be necessary, as is generally the case in the analysis of alloys. In analysis of ores, however, $PbSO_4$ may be contaminated by sulphates of the alkaline earths and by silica. The difficultly soluble oxides of iron and alumina may also be present.

If arsenic is in the sulphate it will pass into the filtrate with the lead.

Determination of Lead as the Chromate, $PbCrO_4$

This excellent method is applicable to a large class of materials and is of special value in precipitation of lead from an acetic acid solution, the method depending upon the insolubility of lead chromate in weak acetic acid.

Procedure. The solution of the sample, precipitation of the lead as the sulphate and extraction of lead with ammonium acetate have been given in detail.

The filtrate, containing all the lead in solution as the acetate, is acidified slightly with acetic acid and heated to boiling. Lead is precipitated by addition of potassium dichromate solution in excess (10 cc. of 5% $K_2Cr_2O_7$ solution are generally sufficient). The solution is boiled until the yellow precipitate turns to a shade of orange or red.[1] The precipitate is allowed to settle until the supernatant solution is clear. (This should appear yellow with the excess of dichromate reagent.) The $PbCrO_4$ is filtered onto an asbestos mat in a tared Gooch cru-

[1] The yellow precipitate gives high results, since it is difficult to wash. The crystalline orange or red compound may be quickly filtered and washed.

cible, washed with water, dried in an oven at about 110° C. and the cooled compound weighed as $PbCrO_4$.

$$PbCrO_4 \times 0.641 = Pb. \quad \frac{Pb. \times 100}{Wt. \text{ of sample}} = \text{per cent Pb.}$$

NOTES. Impurities, such as iron, copper, cadmium, etc., in the acetate solution of lead seriously interfere in the chromate precipitation. These should be leached out with water containing a little sulphuric acid before extracting the lead sulphate with ammonium acetate. See remarks under section on Traces of Lead.

If a standard solution of potassium dichromate is used in the precipitation of lead the excess of the reagent, upon filtering of the precipitate, may be titrated and the lead determined volumetrically. A known amount of dichromate solution (added from a burette) sufficient to precipitate all the lead and about one-third of the volume in excess is added to the hot solution. After boiling about two minutes the precipitate is filtered off quickly and washed several times with hot water. The filtrate, or an aliquot part of it, is made acid with 5 cc. concentrated sulphuric acid and titrated with standard ferrous sulphate at about 60° C., using potassium ferricyanide as an outside indicator; the end-point is a blue color produced by the slight excess of the ferrous salt reacting with the indicator. The excess of dichromate may be determined by adding 3 to 4 grams of solid potassium iodide, KI, to the solution diluted to about 500 cc. with water to which 15 cc. of concentrated sulphuric acid has been added. The liberated iodine is titrated with standard thiosulphate, the end-point being colorless, with starch solution internal indicator, changing from blue. Bi, Sb, Ba, Sr and Ca interfere slightly.

One cc. N/10 $K_2Cr_2O_7$ = 0.010355 gram Pb. One cc. N/5 $K_2Cr_2O_7$ = 0.02071 gram Pb.

Determination of Lead as the Molybdate, $PbMoO_4$

This method is rapid and has the following advantages:

a. The sulphation of lead is avoided. *b*. The acetate extraction is eliminated. *c*. The precipitate may be ignited. *d*. The ratio of lead to its molybdate compound is greater than either lead to $PbSO_4$ or to $PbCrO_4$, lessening the chance of error through weighing.

Cobalt, calcium, strontium and barium have little effect in presence of ammonium acetate. In absence of this salt they interfere slightly.

Procedure. The ore or alloy is decomposed with nitric acid or aqua regia as the case may require. (Silica if present is eliminated by taking to dryness, dehydrating, taking up with dilute nitric acid and filtering.) To the clear liquid ammonium chloride is added and then sufficient ammonium oxalate to destroy the excess of free nitric acid.

Lead is now precipitated by adding 20 to 30 cc. of ammonium molybdate (4 grams per liter+acetic acid) stirring the mixture during the addition. After boiling for two or three minutes the precipitated lead molybdate is allowed to settle, then filtered through pulp, washed with small portions of hot water and ignited over a Bunsen burner.

The cooled residue is weighed as $PbMoO_4$.

$$PbMoO_4 \times 0.5642 = Pb.$$

NOTES. If antimony or other members of the group are present in the original sample it is advisable to dissolve the residue in HCl and reprecipitate the lead with molybdate reagent.

If lead is in the form of the sulphide, as may be the case in a complete analysis of a substance, it is decomposed with hot dilute HNO_3 and precipitated as $PbMoO_4$.

The isolation of minute quantities of lead from large amounts of other substances is described under "Gravimetric Methods for Traces of Lead."

GRAVIMETRIC METHODS

Determination of Lead as the Sulphate, $PbSO_4$

Procedure. The sample having been dissolved according to a method outlined, the lead precipitated as $PbSO_4$ by addition of an excess of sulphuric acid, and taking to SO_3 fumes, the lead sulphate is filtered off, upon cooling and diluting the sample. The $PbSO_4$ is washed with water containing 10% H_2SO_4 until free from soluble impurities. If insoluble sulphates or silica are present the lead must be purified. If such impurities are known to be absent (alloys), the sulphate may be filtered directly onto an asbestos mat in a tared Gooch crucible, dried, then ignited to dull red heat, cooled and finally weighed as $PbSO_4$. In the analysis of ores, however, it is generally advisable to purify the sulphate.

Purification of Lead Sulphate. Details of the procedure have been given under Separations—Extraction of Lead from the Impure Sulphate. The lead sulphate having been brought into solution by extraction with strong ammonium acetate solution, the excess acetic acid is volatilized by evaporation, the residue cooled and diluted with water. An excess of sulphuric acid is added and the precipitated sulphate is filtered off, washed with dilute sulphuric acid and alcohol, dried at about 110° C. and weighed.

$PbSO_4 \times 0.6831 = Pb$. Pb multiplied by 100 and divided by weight of sample taken equals per cent.

NOTES. Lead sulphate may be precipitated from ammonium acetate solution by adding sulphuric acid until the solution contains approximately 10% H_2SO_4.

An acetate extraction may not be necessary, as is generally the case in the analysis of alloys. In analysis of ores, however, $PbSO_4$ may be contaminated by sulphates of the alkaline earths and by silica. The difficultly soluble oxides of iron and alumina may also be present.

If arsenic is in the sulphate it will pass into the filtrate with the lead.

Determination of Lead as the Chromate, $PbCrO_4$

This excellent method is applicable to a large class of materials and is of special value in precipitation of lead from an acetic acid solution, the method depending upon the insolubility of lead chromate in weak acetic acid.

Procedure. The solution of the sample, precipitation of the lead as the sulphate and extraction of lead with ammonium acetate have been given in detail.

The filtrate, containing all the lead in solution as the acetate, is acidified slightly with acetic acid and heated to boiling. Lead is precipitated by addition of potassium dichromate solution in excess (10 cc. of 5% $K_2Cr_2O_7$ solution are generally sufficient). The solution is boiled until the yellow precipitate turns to a shade of orange or red.[1] The precipitate is allowed to settle until the supernatant solution is clear. (This should appear yellow with the excess of dichromate reagent.) The $PbCrO_4$ is filtered onto an asbestos mat in a tared Gooch cru-

[1] The yellow precipitate gives high results, since it is difficult to wash. The crystalline orange or red compound may be quickly filtered and washed.

cible, washed with water, dried in an oven at about 110° C. and the cooled compound weighed as $PbCrO_4$.

$$PbCrO_4 \times 0.641 = Pb. \qquad \frac{Pb. \times 100}{Wt.\ of\ sample} = per\ cent\ Pb.$$

NOTES. Impurities, such as iron, copper, cadmium, etc., in the acetate solution of lead seriously interfere in the chromate precipitation. These should be leached out with water containing a little sulphuric acid before extracting the lead sulphate with ammonium acetate. See remarks under section on Traces of Lead.

If a standard solution of potassium dichromate is used in the precipitation of lead the excess of the reagent, upon filtering of the precipitate, may be titrated and the lead determined volumetrically. A known amount of dichromate solution (added from a burette) sufficient to precipitate all the lead and about one-third of the volume in excess is added to the hot solution. After boiling about two minutes the precipitate is filtered off quickly and washed several times with hot water. The filtrate, or an aliquot part of it, is made acid with 5 cc. concentrated sulphuric acid and titrated with standard ferrous sulphate at about 60° C., using potassium ferricyanide as an outside indicator; the end-point is a blue color produced by the slight excess of the ferrous salt reacting with the indicator. The excess of dichromate may be determined by adding 3 to 4 grams of solid potassium iodide, KI, to the solution diluted to about 500 cc. with water to which 15 cc. of concentrated sulphuric acid has been added. The liberated iodine is titrated with standard thiosulphate, the end-point being colorless, with starch solution internal indicator, changing from blue. Bi, Sb, Ba, Sr and Ca interfere slightly.

One cc. N/10 $K_2Cr_2O_7$ = 0.010355 gram Pb. One cc. N/5 $K_2Cr_2O_7$ = 0.02071 gram Pb.

Determination of Lead as the Molybdate, $PbMoO_4$

This method is rapid and has the following advantages:

a. The sulphation of lead is avoided. *b*. The acetate extraction is eliminated. *c*. The precipitate may be ignited. *d*. The ratio of lead to its molybdate compound is greater than either lead to $PbSO_4$ or to $PbCrO_4$, lessening the chance of error through weighing.

Cobalt, calcium, strontium and barium have little effect in presence of ammonium acetate. In absence of this salt they interfere slightly.

Procedure. The ore or alloy is decomposed with nitric acid or aqua regia as the case may require. (Silica if present is eliminated by taking to dryness, dehydrating, taking up with dilute nitric acid and filtering.) To the clear liquid ammonium chloride is added and then sufficient ammonium oxalate to destroy the excess of free nitric acid.

Lead is now precipitated by adding 20 to 30 cc. of ammonium molybdate (4 grams per liter+acetic acid) stirring the mixture during the addition. After boiling for two or three minutes the precipitated lead molybdate is allowed to settle, then filtered through pulp, washed with small portions of hot water and ignited over a Bunsen burner.

The cooled residue is weighed as $PbMoO_4$.

$$PbMoO_4 \times 0.5642 = Pb.$$

NOTES. If antimony or other members of the group are present in the original sample it is advisable to dissolve the residue in HCl and reprecipitate the lead with molybdate reagent.

If lead is in the form of the sulphide, as may be the case in a complete analysis of a substance, it is decomposed with hot dilute HNO_3 and precipitated as $PbMoO_4$.

Electrolytic Determination of Lead as the Peroxide, PbO_2

An electric current passed through a solution of lead containing sufficient free nitric acid will deposit all the lead on the anode as lead peroxide. The method is excellent for analysis of lead alloys.

Procedure. The sample containing not over 0.5 gram lead is brought into solution by heating with dilute nitric acid, 1 : 1. The solution is washed into a large platinum dish with unpolished inner surface. Twenty to 25 cc. concentrated nitric acid (sp.gr. 1.4) are added and the solution diluted to about 150 cc.

The sample is electrolyzed in the cold with 0.5 to 1 ampere current and 2 to 2.5 volts, the platinum dish forming the anode of the circuit, a spiral platinum wire or a platinum crucible dipped into the solution being the cathode. Three hours are generally sufficient for the deposition of 0.5 gram Pb. Overnight is advisable, a current of 0.05 ampere being used.

A rapid deposition of the lead may be obtained by heating the solution to 60 to 65° C. and electrolyzing with a current $ND_{100} = 1.5$ to 1.7 amperes, the E.M.F. varying within wide limits. Stirring the solution with a rotating cathode aids in the rapid deposition of the PbO_2.

To ascertain whether all the lead has been removed from the solution, more water is added so as to cover a fresh portion of the dish with water. The electrolysis is complete if no fresh deposition of the peroxide takes place after half an hour.

The water is siphoned off while more water is being added until the acid is removed, the current is then broken, the dish emptied of water and the deposits dried at 180° C. and weighed as PbO_2.

The deposit of lead peroxide gently ignited forms lead oxide, PbO, a procedure recommended by W. C. May,[1] confirmed by Treadwell and Hall as giving more accurate results than the peroxide, PbO_2.

$$PbO_2 \times 0.8662 = Pb.$$

$$PbO \times 0.9283 = Pb.$$

NOTE. The deposits of lead oxide or peroxide may be removed by dissolving off with warm dilute nitric acid.

For volumetric procedure-titration of the peroxide PbO_2 see page 240.

VOLUMETRIC METHODS

Volumetric Ferrocyanide Method for the Determination of Lead

Although the gravimetric methods for the determination of lead are considered the more accurate, yet the volumetric procedures may be frequently used with advantage. The ferrocyanide method has been pronounced by Irving C. Bull[2] to be the best of the procedures in common use, the results being accurate.

Procedure. Lead sulphate is obtained according to the method outlined under Preparation and Solution of the Sample. The lead sulphate is transferred to a small beaker and gently boiled with 10 to 15 cc. of a saturated solution of ammonium carbonate, the liquid having been added cold and brought up to

[1] Z. Analyt. Chem., **14**, 347, 1875.
[2] C. N., 2253, **87**, 1903.

boiling. After cooling, the precipitate is filtered onto the original filter paper from which the lead sulphate was removed. The lead carbonate is washed free of alkali with cold water. The filter with the precipitate is dropped into a flask containing a hot mixture of 5 cc. of glacial acetic acid with 25 cc. of water. The lead carbonate is decomposed by boiling and the solution diluted to 150 cc.

Titration. The sample warmed to 60° C. is titrated with a standard solution of potassium ferrocyanide, using a saturated solution of uranium acetate as an outside indicator. The excess of ferrocyanide produces a brown color with the uranium acetate drop on the tile.

Free ammonia must be absent, as it reacts with uranium acetate and gives low results. NH_4OH precipitates reddish brown, gelatinous uranous hydroxide, $U(OH)_4$.

The bulk of solution to be titrated should be as near as possible to 100 cc., including 10 cc. of 50% acetic acid.

One per cent potassium ferrocyanide reagent is used in the titration. This reagent is standardized against a known amount of lead in solution as an acetate.

A correction of 0.8 cc. is generally necessary on account of the indicator. This is determined by a blank titration.

Antimony, bismuth, barium, strontium and calcium interfere only to a very slight extent, the error being negligible.

Volumetric Determination of Lead by the Molybdate Method[1]

Lead is precipitated as molybdate from an acetic acid solution by a standard molybdic solution, the termination of the reaction being recognized by the yellow color produced by the excess of molybdic reagent when a drop of the mixture comes in contact with a drop of tannin solution used as an outside indicator.

Special Reagents Required. ***Ammonium Molybdate Reagent.*** 4.75 grams of the salt are dissolved in water and made up to 1 liter. One cc. with a half gram sample is equal approximately to 1% Pb.

Standardization of Ammonium Molybdate Reagent. 0.293 gram pure lead sulphate, $PbSO_4$, equivalent to 0.2 gram Pb, is dissolved in 50 cc. of a saturated solution of ammonium acetate, a piece of litmus paper is thrown in and a few drops of acetic acid added to acid reaction. The solution is made up to 200 cc. and is titrated as directed below in the procedure for lead.

$$\text{The lead value per cc.} = \frac{0.2}{\text{cc. reagent required}} \text{ gram Pb.}$$

NOTE. In place of $PbSO_4$ pure lead foil may be taken. 0.2 gram of the foil dissolved in 10–15 cc. hot nitric acid 1 : 1 and converted to the sulphate by taking to fumes with 20 cc. 1 : 1 H_2SO_4.

Tannin Indicator. Freshly prepared tannin solution containing 0.1 gram tannin per 20 cc. of water.

Procedure. 0.5 gram of the ore is dissolved by gently heating with 10 cc. of strong hydrochloric acid followed by 5 cc. of nitric acid and additional hydrochloric acid if necessary. Five to 10 cc. of concentrated sulphuric acid are added and the solution evaporated to SO_3 fumes over a free flame. About 25 cc. of

[1] Method of D. H. H. Alexander, modified by Low.

water are added to the cooled solution and the liquid boiled for ten to fifteen minutes to dissolve the anhydrous ferric sulphate that may be present.

Upon cooling, the precipitated $PbSO_4$ with any impurities it may contain (SiO_2, $CaSO_4$, $BaSO_4$, etc.) is filtered off and washed with cold dilute sulphuric acid (1 : 10).

Purification of the Lead Precipitate, in Presence of Calcium, Iron, etc. The precipitate is rinsed into the original flask and about 5 grams of pure ammonium chloride and 1 cc. of concentrated hydrochloric acid added. The solution with the precipitates is boiled until only the silica remains undissolved. The free acid is just neutralized with ammonia and the lead precipitated as PbS by addition of ammonium sulphide. The precipitate is filtered and washed free of calcium. If iron is present it must be removed by redissolving the precipitate in 5 cc. of dilute sulphuric acid and again precipitating the lead as PbS by addition of sufficient hydrogen sulphide water or passing the gas into the acid solution. The lead sulphide is now decomposed by boiling with 5 cc. of concentrated hydrochloric acid for several minutes and then adding 3 or 4 drops of nitric acid to remove the last traces of H_2S.

The free acid in the solution is neutralized with ammonium hydroxide (litmus indicator), and then made slightly acid by addition of glacial acetic acid. The mixture is diluted to 200 cc. with hot water.

Titration. To about two-thirds of the sample, the standard-ammonium molybdate is added from a burette until a drop of the solution, brought into contact with a drop of the tannin indicator upon a white porcelain tile or paraffined paper, gives a brown or yellow color. Some more of the lead solution is added to this titrated sample and the operation is repeated. By keeping a portion of the sample in reserve it is possible to obtain the exact end-point and avoid overrunning, as would be apt to occur if the entire sample were taken at one time.

Cc. molybdate reagent multiplied by value in terms of Pb divided by wt. of sample = Pb.

Blank. Deduction of 0.7 to 1 cc. is frequently necessary. The exact amount may be determined by taking the same amount of reagents as are present in the sample, without the lead, and titrating with ammonium molybdate, as above, on a boiled sample.

Interferences: Antimony, bismuth, barium, strontium and calcium have a slight effect on the results.

The lead is obtained in solution in a comparatively pure form by extraction of the sulphate with ammonium acetate. The more tedious method of isolation as directed in the procedure may not be necessary.

Reduction and Titration of Lead Peroxide Deposited Electrolytically

The electrolytic deposition of lead as the peroxide, PbO_2, has been given on page 238. To avoid error that may result from imperfect drying, a volumetric procedure is suggested. The peroxide is dissolved from the electrode with a hot mixture of 25 cc. N/5 oxalic acid and 10 cc. nitric acid (sp.gr. 1.2). The excess of oxalic acid is titrated hot with N/10 potassium permanganate.

1 cc. N/5 oxalic acid is equivalent to 0.02071 gram lead.

DETERMINATION OF SMALL AMOUNTS OF LEAD

The determination of minute quantities of lead is required in baking powders canned goods and like products in which small amounts of lead are objectionable. Traces of lead ranging from 5 to 100 parts per million (0.0005 to 0.01% Pb) are best determined colorimetrically on 0.5 to 1 gram samples; larger amounts of lead should be determined gravimetrically.

Gravimetric Methods for Determining Traces of Lead

The determination of extremely small amounts of lead cannot be accomplished by the usual methods of precipitation, as the lead compounds remain in solution in a colloidal state. The addition, however, of certain substances, which form amorphous precipitates with the reagents used for throwing out lead causes the removal of lead from the solution by occlusion. For example, the addition of a sufficient quantity of a soluble salt of mercury, copper, or arsenic to a solution containing a trace of lead, and then saturating the solution with H_2S, will cause the complete removal of lead from the solution. Iron and alumina thrown out of the solution as hydroxides will carry down small amounts of lead, and completely remove it from the solution, if they are present in sufficient quantity. Lead may be extracted from finely pulverized substances by means of hot ammonium acetate and precipitated from the extract as lead sulphide. Advantage may be taken of these facts in determining traces of lead in presence of large amounts of other substances.

Amount of the Sample. It is advisable to have the final isolated lead compound over 0.01 gram in weight, hence, in a sample containing 10 parts of lead per million, 800 to 1000 grams of the material should be taken, since a kilogram of the material would contain 0.01 gram, Pb or 0.0156 gram $PbCrO_4$, or 0.01464 gram $PbSO_4$, or 0.0177+ gram $PbMoO_4$. Large samples should be divided into several portions of 100 to 250 grams each, the lead isolated in each, and the final extracts, containing the lead, combined. For the given amount of occluding agent, stated in the procedure, the treated portion should contain not over 0.01 gram lead.

I.—Extraction of Lead with Ammonium Acetate and Subsequent Precipitation

It is frequently desirable to extract the lead from the mass of material and precipitate it from the liquor thus obtained. The procedure worked out by the writer is applicable to determining traces of lead in aluminum salts, but with modifications may be applied to a wide range of substances.

Extraction of Lead. The desired weight of finely powdered substance, in 100-gram portions, is placed in 6-inch porcelain casseroles (1000 cc. capacity). To each portion are added, with vigorous stirring, 500 cc. of *lead-free*, boiling hot ammonium acetate solution (33%).[1] The reaction is apt to be energetic, so that

[1] The reagent must be boiling, when added, to obtain best results. Experiments have shown that considerable alumina and iron dissolve if the proportion of the reagent falls much below 5 cc. of 33% acetate per gram of sample. With twice this amount of reagent the extract is free from iron and alumina. Small amounts of alumina and iron, however, do not interfere in the lead determination.

care must be exercised to avoid boiling over. The residue from aluminum salts is crystalline and may be separated from the extract very readily by filtering through two filter papers in a large Büchner funnel and applying suction.[1] The residue is tamped down to squeeze out the adhering extract and washed with 100 cc. more of hot ammonium acetate followed by 100 to 200 cc. of hot water, again tamped down and sucked as dry as possible. The lead extracts are now combined and lead precipitated as sulphide.

The reagent is made by dissolving one part of lead-free ammonium acetate in two parts of distilled water. The purity of the reagent should be tested.

Precipitation of Small Amounts of Lead. To the solution containing lead is added 2–3 cc. of a 10% copper sulphate or cadmium sulphate reagent. Hydrogen sulphide is passed into the liquor until it is saturated. The copper or cadmium sulphide assists the settling of lead sulphide. Gently warming on the steam bath for half an hour coagulates the precipitate and facilitates settling. The liquor is decanted through a double filter in a small Büchner funnel and the residue washed onto the filter with water saturated with H_2S gas.

The precipitate is washed several times with ammonium sulphide to remove sulphides of the arsenic group and the residue then dissolved in a hot mixture of hydrochloric and nitric acids (1 part HCl, 5 parts HNO_3 and 15 parts H_2O).. Ten cc. of strong sulphuric acid are added to the solution, and the mixture is evaporated to SO_3 fumes *but not to dryness.* The residue is taken up with 100–125 cc. of water containing 2 cc. of sulphuric acid and boiled to dissolve the soluble salts of iron, alumina, copper, etc. After cooling, one-third the volume of 95% alcohol is added (30–40 cc.), the lead sulphate allowed to settle for an hour or more, then filtered and washed several times with 30% alcohol. The residue is extracted with hot ammonium acetate and lead chromate precipitated from the filtrate,[2] made slightly acid with acetic acid, by adding 10 cc. of potassium dichromate reagent and boiling, according to the standard procedure. (Page 236.)

$$PbCrO_4 \times 0.641 = Pb.$$

II.—Precipitation of Lead by Occlusion with Iron Hydroxide

Wilkie found[3] that ferric hydroxide has the property of occluding lead, five parts of $Fe(OH)_3$ removing one part of lead from solution. Advantage is taken of this property of iron hydroxide in precipitating small amounts of lead.[4]

Procedure. The required amount of material is weighed out in 50-gram lots and brushed into No. 8 beakers. If the material contains organic matter, it is treated with 200-cc. portions of concentrated hydrochloric acid, the mixture heated just below the boiling-point of HCl solution, and potassium chlorate added, a few crystals at a time, until the organic matter is decomposed (hood). If the material dissolves in water, the water solution is treated with 5 cc. of concentrated hydrochloric acid and a few crystals of potassium chlorate and the liquor boiled.

[1] 200 to 300 grams of material may be handled in a 6-inch Büchner funnel.

[2] Should lead chromate fail to precipitate, the solution should be treated with H_2S to complete saturation, the sulphide collected on a filter, then dissolved in acid and the procedure described above repeated. If the solution still remains clear, the absence of lead is confirmed.

[3] J. M. Wilkie C. N., 2597, 117, 1909.

[4] Occlusion of lead by zinc sulphide, precipitated by H_2S from a formic acid solution, is suggested; iron and alumina would not interfere.

Addition of Ferric Iron. If sufficient iron is not already present, ferric chloride is added in such quantity that the iron content of the sample will be from twenty to fifty times that of the lead (larger amounts of iron will do no harm) present in the solution. Five to 10 cc. of concentrated nitric acid are added and the sample boiled for ten to fifteen minutes.

Precipitation of Iron and Lead. If alumina is present, iron is precipitated by addition of a large excess of potassium hydroxide, the alumina going into solution as potassium aluminate. In absence of alumina, ammonia may be used to precipitate the ferric hydroxide. Lead is completely occluded by the precipitate and carried down. The solution is filtered hot through Baker and Adamson's fast filters, threefold. The filtering must be rapid and the liquid kept hot to prevent clogging of the filters.

Separation of Lead from Iron. The precipitate is dissolved in hot hydrochloric acid (free from lead). The solutions are combined, if several portions of the sample are taken. Concentrated sulphuric acid is added and the sample evaporated to small volume and heated until the white sulphuric acid fumes appear. The usual procedure is now followed for separation of the lead sulphate, acetate extraction of lead and final precipitation of lead chromate.

$$PbCrO_4 \times 0.641 = Pb.$$

NOTE. In place of using alcohol to decrease the solubility of lead sulphate, many prefer to add sulphuric acid so that the acidity of the solution will be 2–10% free H_2SO_4.

III. Modification of Seeker-Clayton Method for Traces of Lead in Baking Powder

One hundred grams of baking powder are treated with 25 cc. of water followed by 75 cc. of strong hydrochloric acid added in small portions to avoid excess frothing. The mixture is heated until the starch has decomposed (iodine test gives blue color with starch), the solution becoming clear and turning yellow. The free acid is neutralized and when the solution is cold, 400 cc. of lead-free ammonium citrate, saturated with H_2S, are added. Additional H_2S is passed into the slightly alkaline solution, the sulphides of iron and lead allowed to settle, the clear supernatant liquor decanted off, the sulphides collected on a filter and washed. The precipitate is dissolved in nitric acid, lead separated as a sulphate, extracted with acetate and precipitated as dichromate according to the procedure recommended under the acetate extraction method I.[1]

COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF LEAD

Introduction. Estimation of small amounts of lead by the intensity of the brown coloration produced by the sulphide in colloidal solution was first proposed by Pelouze.[2] The procedure was modified by Warington[3] and by Wilkie[4]

[1] See Referee's modification Jour. Assoc. Off. Ag. Chemists, **1**, 3, 512 (Nov., 1915.)
[2] T. J. Pelouze, Ann. Chim. Phys., **3**, 79–108, 1841.
[3] R. Warington, Jour. Soc. Chem. Ind., **12**, 97, 1893.
[4] J. M. Wilkie, Jour. Soc. Chem. Ind., **28**, 636, 1909.

to overcome the color produced by accompanying impurities, among these, of iron, which is almost invariably associated with lead. The method is useful in determining traces of lead in drinking water, in food products, baking powders, canned goods, phosphates, alums, acids such as sulphuric, hydrochloric, citric, tartaric and the like. By this procedure on a gram sample one part of lead per million may be detected and as high as 50 parts may be estimated. For larger amounts of lead, a smaller sample must be taken. Nickel, arsenic, antimony, silver, zinc, tin, iron, and alumina, present in amounts such as commonly occur in these materials, do not interfere.[1]

In order to obtain accurate results it is necessary to have the solutions under comparison possess the same general character. "It must be remembered that the tint depends to a large extent on the size of the colloidal particles of lead, which in turn depend upon the nature of the salts in the solution and upon the way that the solution has been prepared."[2] Vigorous agitation, salts of the alkalies and alkaline earths tend to coagulate the colloidal sulphide.

Reagents Required. ***Standard Lead Solution.*** A convenient solution may be made by dissolving 0.1831 gram of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in 100 cc. of water, clearing any cloudiness with a few drops of acetic acid and diluting to 1000 cc. If 10 cc. of this solution is diluted to 1000 cc. each cc. will contain an equivalent of 0.000001 gram Pb.

Harcourt suggests a permanent standard made by mixing ferric, copper and cobalt salts.[3] For example 12 grams of $FeCl_3$ together with 8 grams of $CuCl_2$ and 4 grams of $Co(NO_3)_2$ are dissolved in water, 400 cc. of hydrochloric acid added and the solution diluted to 4000 cc. 150 cc. of this solution together with 115 cc. of hydrochloric acid (1 : 2) diluted to 2000 cc. will give a shade comparable to that produced by the standard lead solution above, when treated with the sulphide reagent. The exact value per cc. may be obtained by comparison with the lead standard.

Alkaline Tartrate Solution. Twenty-five grams of C.P. sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$, is dissolved in 50 cc. of water. A little ammonia is added and then sodium sulphide solution. After settling some time the reagent is filtered. The filtrate is acidified with hydrochloric acid, boiled free of H_2S and again made ammoniacal and diluted to 100 cc.

Ammonium Citrate Solution. Ammonium citrate solution is prepared in the same way as the tartrate solution above, 25 grams of the salt being dissolved in 50 cc. of water.

Potassium Cyanide. Ten per cent solution. The salt should be lead-free.

Sodium Sulphide. Ten per cent solution, made from colorless crystals. Sodium sulphide may be made by saturating a strong solution of sodium hydroxide with hydrogen sulphide gas, and then adding an equal volume of the sodium hydroxide. The solution is diluted to required volume, allowed to stand several days, and filtered.

Sodium metabisulphite. Solid salt of $Na_2S_2O_5$.[4]

Apparatus. The color comparison may be made in Nessler tubes, or in a colorimeter. The Campbell and Hurley modification of the Kennicott-Sargent

[1] Ni up to 0.1%, As up to 0.2%, Zn 0.2%, Sb 0.05%, Cu 0.25%, Fe 1.0%, Al 10%, Sn up to 1.4% do not interfere.

[2] J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis."

[3] A. G. V. Harcourt, Jour. Chem. Soc., **97**, 841, 1900.

[4] Recommended by W. S. Allen for reduction of iron.

colorimeter is excellent for this purpose,[1] Fig. 43. The colorimeter is simple in construction and operation.

The tubes for holding the solutions to be compared are those of one of the well-known colorimeters, in which the unknown solution is placed in the left-hand tube while the color is matched by raising or lowering the level of a standard solution in the right-hand tube by means of a glass plunger working in an attached reservoir.

The accompanying diagram shows the essential features of construction of the colorimeter employed in the tests described below. The unknown solution is placed in the left-hand tube *A*, which is 19 cm. long, 3 cm. in diameter, and graduated for 15 cm. The standard solution is placed in the right-hand tube *B*, which is the same size as *A*, the graduated portion being divided into 100 divisions of 1.5 mm. each. The tube *B* is permanently connected by a glass tube with the reservoir *C* in which the glass plunger *D* works, so that the level of the liquid in *B* can be readily controlled by raising or lowering the plunger. As the tube *B* and reservoir *C* are made in one piece, the liquid used for the standard solution comes in contact with glass only, thus preventing any possibility of chemical change due to contact with the container. The plunger is provided with a rubber collar *E*, so placed as to prevent the plunger from accidentally striking and breaking the bottom of the reservoir. The tubes *A* and *B*, with the connecting reservoir, rest on wooden supports, the one under *A* and *B* being provided with holes for the passage of the light, and are held in position by spring clips *F F*. This arrangement allows the glass parts to be readily removed for cleaning and filling. The light for illuminating the solution is reflected upward through the tubes *A* and *B* by means of the adjustable mirror *G*. The best results are obtained by facing the colorimeter toward a north window in order to get reflected skylight through the tubes, care being taken to avoid light reflected from adjacent objects. The black wooden back of the colorimeter serves the double purpose of a support for the parts of the instrument and of a screen, as it is interposed between the color tubes and the source of light.

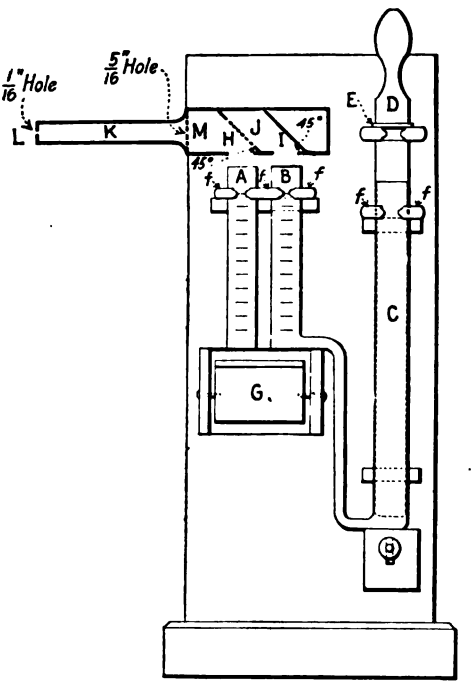


FIG. 43.—Hurley's Colorimeter.

The light, passing upward through the tubes *A* and *B*, impinges on the two mirrors *H* and *I* cemented to brass plates sliding in grooves cut at an angle of 45° in the sides of the wooden box *J*. This box is supplied with a loosely-fitting cover, thus allowing easy access for the purpose of removing and cleaning the

[1] Jour. Am. Chem. Soc., **33**, 1112, July, 1911.

mirrors. The mirror *H* is cut vertically and cemented in such a position as to reflect one-half of the circular field of light coming through the tube *A*. The light passing upward through *B* is reflected horizontally by the mirror *I*, through a hole in the brass plate supporting the mirror *H*. One-half of the circular field of light from the tube *B* is cut off by the mirror *H*, the vertical edge of which acts as a dividing line between the two halves of the circular field. The image of one-half of the tube *B* is then observed in juxtaposition to the opposite half of the image of the tube *A*.

The juxtaposed images are observed through a tube *K*, 2.5 cm. in diameter and 16 cm. long, lined with black felt and provided with an eye-piece having a hole 1.5 mm. in diameter. At the point *M* in the tube *K* is placed a diaphragm having an aperture 8 mm. in diameter. All parts inside the box *J* except the mirrors are painted black so that no light except that coming through the tubes *A* and *B* passes through the tube *K*. By having the apertures in the eye-piece and diaphragm properly proportioned only the image of the bottoms of the tubes *A* and *B* can be seen, thus preventing interference of light reflected from the vertical sides of the tubes *A* and *B*.

A person looking through the eye-piece observes a single circular field divided vertically by an almost imperceptible line when the two solutions are of the same intensity. By manipulating the plunger *D*, the level of the liquid in *B* can be easily raised or lowered, thus causing the right half of the image to assume a darker or lighter shade at will. In matching colors with an ascending column in *B*, that is, gradually deepening the color of the right half of the field, the usual tendency is to stop a little below the true reading while in a comparison with a descending column the opposite is the case.

Procedure. If lead is between 10 to 50 parts per million a 1-gram sample is taken. If it is above or below these extremes the amount of sample is regulated accordingly. In materials containing organic matter it is not advisable to take more than a 1-gram sample.

Substances containing organic matter, such as starch in baking powder, should be decomposed by fusion with sodium peroxide, sodium or potassium sulphate containing a few drops of sulphuric acid. A Kjeldahl digestion with concentrated sulphuric acid and potassium bisulphate may occasionally be advisable. Sulphuric acid discolored by organic matter should be mixed with 4 to 5 grams of potassium bisulphate, taken to fumes and then diluted with water. The material may be extracted with ammonium acetate and lead determined in the extract. See notes.

To the solution containing the sample are added 10 cc. of tartrate solution (or 20 cc. of citrate solution with phosphates of lime, etc.), 10 cc. of hydrochloric acid and the mixture brought to boiling. Small amounts of ferric iron are now reduced by adding 0.5 gram sodium metabisulphite. Sufficient ammonium hydroxide is added to neutralize the free acid and 5 cc. in excess; then 3 cc. potassium cyanide (to repress any copper color that may be present to reduce higher oxides), and the mixture heated until the solution becomes colorless. The entire solution or an aliquot portion is placed in the comparison cylinder, and diluted to nearly 100 cc. If the Kennicott-Sargent apparatus is used the standard color solution is forced into the adjacent cylinder, until the color in this cylinder matches the one containing the sample. The number of cc. of the standard is noted. This blank is due to the slight color that the solutions of the samples invariably have. Four drops of the sulphide reagent are added to the sample and this is mixed

by means of a plunger, avoiding any more agitation than is absolutely necessary to make the solution homogeneous. After one minute the comparison is again made, the colored standard being forced into the cylinder until its color matches the sample. It is advisable to take several readings with ascending and descending column of standard reagent, taking the average as the true reading.

Calculation. Suppose the standard = 0.000001 gram Pb per cc., blank = 5 cc., total reading = 22 cc., one gram of sample being taken for analysis. Then 22 − 5 = 17 cc. = 0.0017% Pb or 17 parts per million.

NOTES. Iron must be completely reduced before adding ammonium hydroxide and potassium cyanide.

Allen's method of reducing iron with sodium metabisulphate is excellent. The salt may be made by passing SO_2 into a saturated solution of sodium carbonate at boiling temperature, until the liquor is just acid to methyl orange. The water evaporated during the treatment is replaced during the action. $Na_2S_2O_5$ separates and may be filtered off and the water removed by centrifuging.

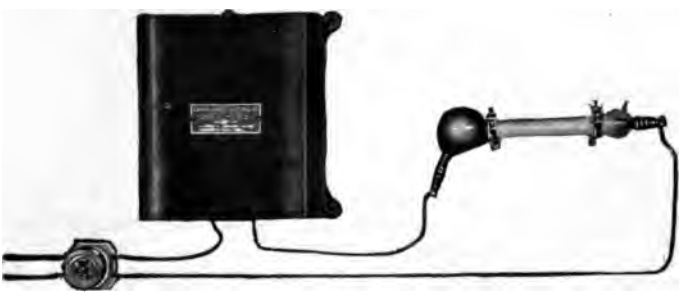


FIG. 44.—Cooper Hewitt Mercury Light.

The Cooper Hewitt Mercury light is excellent for colorimetric lead determinations, where an artificial light is desired. The yellow shades appear yellowish-green and may be matched more readily than the yellows obtained by daylight.

The illustration, Fig. 44, shows the type of light recommended for this work.

If a separation from iron is desired, the lead may be extracted with ammonium acetate solution. Ten grams of the powdered material are mixed with 75 cc. of a 33% ammonium acetate solution [1] (25 grams of the salt dissolved in 50 cc. H_2O), the reagent being added boiling hot. The mixture is diluted to 500 cc., a portion filtered, and the determination made on an aliquot part of the total, following the directions above.

[1] The ammonium acetate should be free from lead.

ANALYSIS OF METALLIC LEAD

Determination of Impurities in Pig Lead—Complete Analysis [1]

The following substances are generally estimated in the complete analysis of lead: silver, bismuth, copper, cadmium, arsenic, antimony, tin, iron, cobalt, nickel, manganese and zinc.

Determination of Silver

This is determined by assay of 100 grams of lead. The substance is placed in a 3-in. scorifier and heated in a muffle furnace until the assay "covers." It is then poured into a mould, allowed to cool and the button thus obtained again scorified until a final button weighing about 20 grams is obtained. This is cupeled and silver determined as usual. If the silver bead is large it should be parted for gold.

Determination of Bismuth

In determining bismuth three cases arise: *A*. The ordinary method. *B*. Procedure for determining minute amounts of bismuth. *C*. Method in presence of comparatively large amounts of antimony and tin.

A. Twenty grams of lead are dissolved in 100 cc. of hot dilute nitric acid (1 : 4). If the solution is complete, dilute ammonium hydroxide is added, drop by drop, until a faint opalescence is observed in the solution. If a precipitate is formed, this must be dissolved by addition of nitric acid and the ammonia treatment repeated. Now 5 cc. of dilute hydrochloric acid are added (1 : 9) and the solution diluted to 400 cc. and heated to boiling. The bismuth oxychloride is allowed to settle on the steam bath for several hours, the clear solution is then decanted through a 7 cm. filter (S. & S. No. 589), the precipitate transferred to the paper and washed with hot water. (The solution is refiltered if cloudy.) The precipitate is dissolved with 5 cc. of hydrochloric acid (1 : 2), the acid being added around the edge of the filter with a pipette. The paper is washed and the solution diluted to 300 cc. and brought to boiling. The precipitate is filtered into a weighed Gooch crucible, washed several times with water, then once with alcohol and finally with ether. It is dried in the oven and weighed as BiOCl.

$$BiOCl \times .802 = Bi.$$

B. Determination of minute amounts of bismuth is made as follows: 100 grams of lead are dissolved in 500 cc. of dilute nitric acid (1 : 4), and the cooled solution treated with sufficient saturated solution of sodium carbonate to produce a heavy precipitate. After settling, then decanting off the clear solution, the precipitate is filtered onto a filter and drained. Without washing this is dissolved with the least amount of nitric acid that is required. The solution is then neutralized with ammonia as before (method *A*), litmus paper being used as an indicator, and bismuth determined as directed under the first procedure.

C. In presence of considerable amounts of antimony and tin, the bismuth is precipitated as in case *A*, the precipitate dissolved in hot hydrochloric acid (1 : 2), and the solution diluted to 200 cc. The sulphides of antimony, tin, etc.,

[1] Method of the National Lead Company, modified.

are precipitated with H_2S, antimony and tin dissolved out with a solution of potassium hydroxide and sulphide water (1 part 20% KOH to 4 parts H_2S water), and the residue washed. This is dissolved in 20 cc. of hot nitric acid (1 : 4), and bismuth determined as usual in the filtrate.

Determination of the Remaining Elements

222.23 grams of the sample of lead are dissolved in 1100 cc. of dilute nitric acid (1 : 4) in a large beaker. If the solution is turbid, appreciable amounts of antimony and tin are indicated with possible sulphur combined as $PbSO_4$. In this case it is filtered into a 2000-cc. flask. If the solution is clear it is transferred directly to the flask.

Residue I. May contain As, Sb, Sn, $PbSO_4$.

Filtrate I. Contains all the elements present in the sample.

Residue I. The residue and filter is treated with 20 cc. of tartaric acid mixture (50 grams tartaric acid, 250 cc. of water and 250 cc. of concentrated hydrochloric acid). After boiling the mixture is digested on the steam bath for half an hour, then 50 cc. of hot water added and the solution filtered. The filter paper is ignited and any residue is dissolved by fusion with 1 gram of potassium hydroxide in a silver dish. The water extract of this fusion is added to the tartrate solution. Now ammonia is added until the solution is alkaline and then hydrochloric acid until it is slightly acid. Hydrogen sulphide is now passed in to saturation, the precipitate digested on the steam bath for fifteen to twenty minutes and hydrogen sulphide again passed into the solution about fifteen minutes. The sulphides are filtered off, arsenic, antimony and tin sulphides dissolved with 5 cc. (1 : 5) potassium hydroxide in 25 cc. of saturated H_2S water. The solution is diluted to 111 cc., and 100 cc.—equivalent to 200 grams of sample—preserved for subsequent analysis. This solution is marked " Extract C."

Filtrate I. This solution, containing practically all of the material, is treated with 150 cc. of dilute sulphuric acid (1 : 1), and the solution made to volume—2000 cc. It is now transferred to a 3-liter flask, the graduated flask rinsed out into the main solution with 50 cc. of water. (The $PbSO_4$ precipitate found to occupy space of 50 cc.) When the precipitate has settled, 1800 cc. are decanted off. This represents 200 grams of the sample. The solution is boiled down in a No. 9 porcelain evaporating dish, heating first over the free flame and finally on the steam bath until only a moist residue remains. Fifty cc. of water is added, the residue transferred to a beaker and digested for several hours, preferably overnight, and then filtered.

Residue II. This may contain $PbSO_4$, As, Sb, Sn salts.

Filtrate II. This may contain Cu, Bi, Cd, Sn, Sb, As, Fe, Co, Ni and Zn.

Residue II. This is treated as has been described for residue I. The entire solution is added to the Extract C. The residue, consisting of $PbSO_4$, is rejected.

Filtrate II. This is made neutral with ammonium hydroxide and then concentrated hydrochloric acid added in such an amount that the solution will contain 4% free acid. (HCl sp.gr. 1.2, 4 cc. per 100 of solution.) Hydrogen sulphide is now passed into the hot solution until it is saturated, the precipitate

settled on the steam bath for half an hour and hydrogen sulphide again passed in for fifteen minutes. The precipitate is filtered off and washed with H_2S water slightly acidified with hydrochloric acid.

Residue III. May contain CuS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS.

Filtrate III. May contain ions of Fe, Al, Co, Ni, Mn and Zn. This filtrate is marked "B."

Residue III. The sulphides are extracted with potassium hydroxide and hydrogen sulphide solution. This dissolves out arsenic, antimony and tin. This extract is combined with the extract marked "C."

The residue remaining is marked "Residue A."

The constituents of the sample have now been isolated in the groups.

Residue "A" contains the sulphides of copper, bismuth and cadmium.

Filtrate "B" contains such elements as do not precipitate as sulphides in acid solution—iron, aluminum, manganese, cobalt, nickel and zinc.

Extract "C" includes the elements arsenic, antimony and tin.

Determination of Arsenic, Antimony, and Tin in Pig Lead

The combined alkali sulphide solutions: "Extract C" is washed into a beaker and acidified with 20 cc. of nitric acid and 5 cc. of hydrochloric acid. The solution is evaporated to dryness on the steam bath. The residue is dissolved in 200 cc. of water and 10 grams of oxalic acid added, together with 10 grams of ammonium oxalate, and the solution heated until clear.

Hydrogen sulphide gas is now passed into the hot solution for forty-five minutes.

Precipitate. As_2S_3, Sb_2S_3. **Filtrate** contains Sn.

Arsenic. The precipitate containing arsenic and antimony is placed in a distilling flask, strong hydrochloric acid added and arsenic separated from antimony by distillation with a current of HCl gas according to the regular procedure. If a precipitate of arsenic sulphide forms in the distillate, it is advisable to precipitate the arsenic as sulphide, oxidize the compound to form sulphate and arsenic acid, and after reduction of the arsenic to titrate it with standard iodine. This oxidation may be accomplished, before distillation with hydrochloric acid. For details of the procedure see chapter on Arsenic, page 33.

Antimony is determined in the residue in the flask by titration with N/10 potassium bromate or by the potassium iodide method.

I. $2KBrO_3+2HCl+3Sb_2O_3=2KCl+2IIBr+3Sb_2O_5$.

II. (*a*) $Sb_2Cl_5+2KI=Sb_2Cl_3+2KCl+I_2$.

(*b*) $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$.

For details of the procedure see chapter on Antimony, pages 25 and 26.

Determination of Copper and Cadmium in Pig Lead

The residue "A" is taken for this analysis. If copper exceeds 0.0025% method I is used. If the copper percentage is below this amount the procedure II is followed.

Method I. The residue is dissolved by heating with 20 cc. of nitric acid (1 : 4) and the solution filtered into a beaker. The filter is ignited and the residue dissolved in nitric acid (1 : 1) and the solution added to the first portion. The volume should not exceed 100 cc. Ammonium hydroxide is added until the solution is strongly ammoniacal and then 5 grams of potassium cyanide. Hydrogen sulphide is passed into the cold solution to saturation, and the solution filtered.

Precipitate = AgS, Bi_2S_3, CdS. **Filtrate** = Cu in solution.

The filtrate containing the copper is evaporated on the steam bath to a volume of 20 to 30 cc. in a 4-in. casserole. Now 20 cc. of sulphuric acid (1 : 1) are added (hood), and the solution evaporated until SO_3 fumes are evolved. The cooled concentrate is diluted with water and filtered, if necessary. Three cc. of nitric acid are added per 100 cc. of solution and the copper deposited by electrolysis according to the regular procedure and weighed as metallic copper. For detailed method see chapter on Copper, page 155.

The precipitate containing silver, bismuth and cadmium is dissolved in 20 cc. of nitric acid (1 : 4), 1 cc. of 1% sodium chloride solution is added, the solution digested half an hour and then filtered and the filter washed with water.

Precipitate – **AgCl**, reject. **Filtrate** – $Cd(NO_3)_2$ and $Bi(NO_3)_3$.

The filtrate is made slightly alkaline with sodium carbonate added in slight excess, and 5 grams of potassium cyanide are then added. After digesting on the steam bath for half an hour the solution is filtered and the residue washed with 5% sodium carbonate solution.

Precipitate contains bismuth, reject. **Filtrate** contains cadmium.

The filtrate is now treated with a few cc. of ammonium sulphide and the yellow cadmium sulphide is filtered into a weighed Gooch crucible, then washed, dried and finally weighed as CdS.

$$CdS \times 0.778 = Cd.$$

Method II. Small amounts of copper. The filter containing the sulphides is ignited in a porcelain crucible and the residue dissolved in 5 to 10 cc. of nitric acid (1 : 1), and the solution evaporated to pastiness. One cc. of sulphuric acid (1 : 1) is added together with a few drops of 10% sodium chloride solution and the mixture evaporated to SO_3 fumes, the cooled product then diluted with water and filtered from the lead and silver precipitates.

Ammonia is now added to the filtrate together with 5 grams of potassium cyanide and CdS and Bi_2S_3 are precipitated with H_2S, as in case I, and filtered off.

Precipitate—CdS and Bi_2S_3. Bismuth is removed as before and cadmium sulphide again precipitated and the compound titrated with N/10 iodine solution.

1 cc. N/10 I = 0.00562 gram Cd.

Filtrate. The solution is made acid in the hood with H_2SO_4, then taken to SO_3 fumes and copper determined by the potassium iodide method.

Determination of Iron, Cobalt, Nickel, Manganese and Zinc in Pig Lead

Iron and Alumina. The filtrate " B " from members of the Hydrogen Sulphide Group is evaporated to 100 and the iron oxidized with a few drops of nitric acid as usual. Iron (and alumina) hydroxide is now precipitated by addition of ammonia. It is advisable to dissolve this precipitate in hydrochloric acid and reprecipitate the iron to recover the occluded manganese and zinc. The combined filtrates are reserved for the determination of the remainder of the elements. The hydroxide of iron is ignited and weighed as Fe_2O_3. If alumina is suspected, the residue is dissolved in hydrochloric acid and iron determined volumetrically. Fe_2O_3 thus obtained is subtracted from the weight of the first determination. the difference being due to the alumina present.

$$Fe_2O_3 \times 0.6994 = Fe \qquad \text{Reciprocal factor} = 1.4298$$

$$Al_2O_3 \times 0.5303 = Al \qquad \text{Reciprocal factor} = 1.8856$$

Zinc. The filtrate from iron precipitate is made neutral with hydrochloric acid and then 15 drops of 2N. HCl added in excess and zinc precipitated in the pressure flask with H_2S. (See Figs. 3 and 4 in chapter on Arsenic.) The sulphide of zinc is filtered off, and either ignited to the oxide ZnO and so weighed or determined by a volumetric procedure. See chapter on Zinc.

$$ZnO \times 0.8034 = Zn.$$

$$H_2SO_4 \times 0.6665 = Zn.$$

Cobalt and Nickel. These are best determined by electrolysis, being deposited from an ammonium sulphate solution according to the procedure described for these elements.

If a separation of the elements is desired the deposit is dissolved in acid, nickel determined by O. Brunck's dimethylglyoxime method, and cobalt determined by difference.

Manganese. The solution from nickel and cobalt is taken to dryness, and the residue heated to expel the ammonium salts and destroy any organic matter present. This is taken up with a little hydrochloric acid, then 2 to 3 cc. of sulphuric acid added and the mixture evaporated to SO_3 fumes to expel the hydrochloric acid. When nearly all the free acid is driven off, the moist residue, cooled, is treated with 50 cc. of nitric acid (1 : 3), and manganese determined in the solution preferably by the bismuthate method. For minute amounts of manganese the colorimetric procedure is used. See chapter on Manganese, page 267.

MAGNESIUM

WILFRED W. SCOTT

Mg, *at.wt.* 24.32; *sp.gr.* 1.69–1.75; m.p. 651° [1]**; *b.p.* 1120° C.**[2]**; oxide MgO.**

DETECTION

In the usual course of analysis magnesium is found in the filtrate from the precipitated carbonates of barium, calcium, and strontium. The general procedure for removal of the preceding groups may be found in the section on Separations given on the following page, 254. Magnesium is precipitated as white magnesium ammonium phosphate, $MgNH_4PO_4$, by an alkali phosphate, Na_2HPO_4, $NaNH_4HPO_4$, etc., in presence of ammonium chloride and free ammonia. The precipitate forms slowly in dilute solution. This is hastened by agitation and by rubbing the sides of the beaker during the stirring with a glass rod. Crystals soon appear on the sides of the beaker in the path of contact, and finally in the solution.

Baryta or lime water added to a solution containing magnesium produces a white precipitate of magnesium hydroxide.

Both the phosphate and the hydroxide of magnesium are soluble in acids.

ESTIMATION

The element is determined in the complete analysis of a large number of substances; in the analysis of ores, minerals, rocks, soils, cements, water, etc. The following are the more important ores in which the element occurs: Magnesite, $MgCO_3$; dolomite, $CaCO_3 \cdot MgCO_3$; kieserite, $MgSO_4 \cdot H_2O$; kainite, $MgSO_4 \cdot KCl \cdot 6H_2O$; carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$; in the silicates, enstatite, $MgSiO_3$; talc, $H_2Mg_3(SiO_3)_4$; meerschaum, forsterite, Mg_2SiO_4; titanate, $MgTiO_3$; olivine, $Mg_2SiO_4 \cdot Fe_2SiO_4$; serpentine, $H_4Mg_3Si_2O_9$. It occurs as boracite, $4MgB_4O_7 \cdot 2MgO \cdot MgCl_2$. It is found in sea-water, and in certain mineral waters. It occurs as a phosphate and carbonate in the vegetable and animal kingdoms, especially in seeds and bones.

Preparation and Solution of the Sample

In solution of the material it will be recalled that the metal is soluble in acids and is also attacked by the acid alkali carbonates. It is soluble in ammonium salts. The oxide, hydroxide, and the salts of magnesium are soluble in acids. Combined in silicates, however, the substance requires fusion with alkali carbonates to bring it into solution.

General Procedure for Ores. One gram of the ore is treated with 20 cc. of strong hydrochloric acid and heated gently until the material is decomposed. If sulphides are present, 5 to 10 cc. of strong nitric acid are added and the material decomposed by the mixed acids. If silicates are present and the decompo-

[1] Circular 35 (2d Ed.) U. S. Bureau of Standards.
[2] Van Nostrand's Chem. Annual—Olsen.

sition is not complete by the acid treatment, the insoluble material is decomposed by fusion with sodium carbonate, or the entire sample may be fused with the alkali carbonate, the fusion is dissolved in hydrochloric acid and taken to dryness. Silica is dehydrated as usual by heating the residue from the evaporated solution. This is taken up with 50 cc. of water containing about 5 cc. strong hydrochloric acid, the silica filtered off and, after removal of the interfering substances according to procedures given under the next section on Separations, magnesium is determined as directed in the sections on Methods.

SEPARATIONS

Removal of Members of the Hydrogen Sulphide Group. Copper, Lead, Bismuth, Cadmium, Arsenic, etc. The filtrate from silica[1] is diluted to about 200 cc. and hydrogen sulphide gas passed in until the members of this group are completely precipitated. The sulphides are filtered off and washed with H_2S water and the filtrate and washings concentrated by boiling. This treatment is seldom necessary in analysis of many silicates and carbonates in which these elements are absent.

Removal of Iron, Aluminum, Manganese, Zinc, etc. The concentrated filtrate from the hydrogen sulphide group, or in case the treatment with hydrogen sulphide was not required, the filtrate from silica, is boiled with a few cc. of nitric acid to oxidize the iron (solution turns yellow), about 5 cc. of concentrated hydrochloric acid added, and if manganese is present, 15 to 20 cc. of a saturated solution of bromine water, and the solution made alkaline to precipitate iron, aluminum, manganese. If zinc, cobalt, and nickel are present, these are best removed as sulphides by passing hydrogen sulphide into the ammoniacal solution under pressure. (See Fig. 3 and Fig. 4, pages 38 and 39.)

Separation of Magnesium from the Alkaline Earths. The alkaline earths are precipitated either as oxalates, recommended when considerable calcium is present, or as sulphates, recommended in presence of a large proportion of barium, the magnesium salts being soluble. Magnesium is precipitated from the filtrates as a phosphate, according to directions given later. Details of the separation of magnesium from the alkaline earths may be found in the chapter on Barium, page 53.

An excellent procedure for the separation by means of sulphuric acid is to evaporate the solution to dryness, concentrating first in a porcelain dish and finally to dryness in a platinum dish, and then adding about 50 cc. of 80% alcohol and sufficient sulphuric acid to combine with the alkaline earths and magnesium, with slight excess. This precipitates barium, strontium, and calcium as sulphates, while the greater part of the magnesium is in solution. After settling, the precipitate is filtered and washed free of sulphuric acid by means of absolute alcohol, then with 40% alcohol to remove any magnesium sulphate remaining with the precipitate. Magnesium is determined in the filtrate by expelling the alcohol by evaporation, and then precipitating as magnesium ammonium phosphate according to directions given for the determination of this element.

NOTE. Magnesium is prevented from precipitation as a hydroxide by ammonia by the presence of ammonium salts, the complex salt $(NH_4)_2MgCl_4$, being formed, which is readily soluble.

[1] See previous paragraph.

GRAVIMETRIC DETERMINATION OF MAGNESIUM

Precipitation of Magnesium by a Soluble Phosphate as Ammonium Magnesium Phosphate

Magnesium is determined in the filtrate from calcium oxalate by the addition of sodium ammonium phosphate to a hot slightly acid or neutral solution followed by a definite amount of ammonia. The practice of precipitating magnesium from a cold solution necessitates a double precipitation as the composition of the phosphate is considerably modified by that of the solution in which the precipitation takes place, so that it is necessary to adjust conditions by having a definite amount of ammonia, ammonium salts and phosphate for the approximate amount of magnesium present.[1] Accurate results are obtained by precipitation of the compound from a hot solution by the method of B. Schmitz,[2] by addition of the soluble phosphate to a slightly acid solution and then making ammoniacal, or that of W. Gibbs,[3] by precipitation of the amorphous magnesium hydrogen phosphate in a neutral solution and transforming the precipitate to magnesium ammonium phosphate by addition of ammonia to the hot solution. Upon ignition of the precipitate, magnesium pyrophosphate ($Mg_2P_2O_7$) is formed.

Precipitation Reactions.

A. $Na_2NH_4PO_4 + MgCl_2 = 2NaCl + MgNH_4PO_4$ (B. Schmitz).

B. $NaHNH_4PO_4 + MgCl_2 = NaCl + NH_4Cl + MgHPO_4$ and

$MgHPO_4 + NH_3 = MgNH_4PO_4$ (W. Gibbs).

Decomposition with Heat.

$2MgNH_4PO_4 = 2NH_3 + H_2O + Mg_2P_2O_7$.

Procedure. The acid or neutral solution containing magnesium in presence of ammonium salts is heated to boiling and is treated with an excess of sodium or ammonium phosphate, or with a normal solution of microcosmic salt, $NaHNH_4PO_4 \cdot H_2O$, stirring constantly during the addition. Then while agitating, one-third the volume of 10% ammonium hydroxide is added.

The crystalline precipitate is allowed to settle and cool for two or three hours, the supernatant liquid is filtered off and the precipitate washed three times by decantation with 2.5% ammonia. The precipitate is dried and then transferred as completely as possible to a weighed platinum crucible, the ash of the filter paper, burned separately, is added and the compound heated gently at first, the crucible being covered until the ammonia is driven off, and then more strongly until the mass is snow white. The residue is cooled in a desiccator and weighed as $Mg_2P_2O_7$. The ammonium magnesium phosphate may be filtered directly into a weighed Gooch crucible and ignited, thus avoiding the carbon of the filter paper, and shortening the period of ignition, less heat being required to obtain the white magnesium pyrophosphate.

[1] F. A. Gooch and M. Austin, Am. Jour. Sci. (4), **7**, 187, 1899. W. Gibbs, C. N., **28**, 51, 1873. H. Struve, Zeit. anal. Chem., **36**, 289, 1897.

[2] Z. anal. Chem., **512**, 1906.

[3] Am. Jour. Sci. (3), **5**, 114, 1873.

Factors.[1] $Mg_2P_2O_7 \times 0.3621 = MgO$ or $0.2184 = Mg$ or $\times 0.7572 = MgCO_3$ or $\times 1.0811 = MgSO_4$ or $\times 2.2143 = MgSO_4 \cdot 7H_2O$.

Notes on Magnesium

The ignition is conducted gently at first to gradually oxidize the carbon that the precipitate contains. With rapid ignition the particles are inclosed in the mass in a form that it is almost impossible to completely oxidize, so that the final residue is gray instead of white. L. L. de Koninck[2] considers that the blackening of the precipitate is frequently due to the presence of organic bases in commercial ammonia and its salts, rather than to the fibers of filter paper occluded in the mass. With caution, the filter and residue may be ignited wet, the heat being low until the filter completely chars and then being increased, with the cover removed, until the residue is white.

Impurities. The precipitate may contain traces of lime that remained soluble in ammonium oxalate. This may be determined by dissolving the pyrophosphate in dilute sulphuric acid followed by addition of 9 to 10 volumes of absolute alcohol. Calcium sulphate, $CaSO_4$, precipitates and settles out on standing several hours. It may be filtered off, dissolved in hydrochloric acid and precipitated as oxalate in the usual way and so determined.

A residue remaining after treating the pyrophosphate with acid is generally SiO_2.

The presence of manganese may be detected by dissolving the magnesium pyrophosphate, $Mg_2P_2O_7$, in nitric acid and oxidizing with sodium bismuthate. (See method under Manganese.)

Properties of Ammonium Magnesium Phosphate. Readily soluble in dilute acids. One hundred cc. of pure water at 10° C. will dissolve 0.0065 gram. The presence of ammonia greatly decreases the solubility of the salt, e.g., 2.5% ammonia decreases the solubility to 0.00006 gram MgO per 100 cc. The presence of ammonium salts increase the solubility of the precipitate, e.g., 1 gram of ammonium chloride will increase the solubility to 0.0013 gram MgO.[3]

VOLUMETRIC DETERMINATION OF MAGNESIUM

Titration of the Ammonium Magnesium Phosphate with Standard Acid

The procedure known as Handy's volumetric method for magnesium,[4] depends upon the reaction $MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4$. An excess of standard sulphuric acid is added to the precipitate and the excess of acid titrated back with standard ammonium hydroxide.

Procedure. The method of precipitation of the magnesium ammonium phosphate is the same as has been described under the gravimetric method. The precipitate is washed several times by decantation with 10% ammonium hydroxide solution (1 part NH_4OH, sp.gr. 0.90 to 9 parts water), and finally on the filter. After draining, the filter is opened out, the moisture removed as much as possible by means of dry filter papers. The residue may be dried in the room for about forty-five minutes or in the air oven at 50 to 60° C. for fifteen to twenty minutes.[5] When the filter has dried, ammonia will have been expelled. The substance is placed in a dry beaker, N/10 sulphuric acid added in excess (methyl orange indicator), the solution diluted to 100 cc. and the excess of acid titrated with N/10 sodium hydroxide.

One cc. N/10 $H_2SO_4 = 0.002$ gram MgO.

[1] Based on atomic weights of 1916.
[2] Zeit. analy. Chem., **29**, 165, 1890.
[3] Mellor, "Quantitative Inorganic Analysis," J. B. Lippincott Co., Pub.
[4] James Otis Handy, Jour. Am. Chem. Soc., **22**, 31.
[5] Low, "Technical Methods of Ore Analysis," Wiley & Sons, Pub.

MANGANESE

WILFRED W. SCOTT

Mn, *at.wt.* 54.93; *sp.gr.* 7.42[1]; *m.p.* 1260°[2]; *b.p.* 1900° C[1]; *oxides*, MnO, Mn_2O_3, (Mn_3O_4 *ignition in air*), MnO_2, MnO_3, Mn_2O_7.

DETECTION

In the usual course of analysis manganese is found in the filtrate from the hydroxides of iron, aluminum and chromium, the previous groups having been removed with hydrochloric acid, hydrogen sulphide and ammonium hydroxide in presence of ammonium chloride. Manganese, cobalt, nickel and zinc are precipitated as sulphides in an ammoniacal solution. The sulphides of manganese and zinc are dissolved by cold dilute hydrochloric acid, H_2S expelled by boiling and manganese precipitated as the hydroxide by addition of potassium hydroxide in sufficient amount to dissolve the zinc (sodium zincate). Manganese is now confirmed by dissolving this precipitate in nitric acid and adding red lead or lead peroxide to the strong nitric acid solution. A violet-colored solution is produced in presence of manganese. Chlorides should be absent.

Manganese in soils, minerals, vegetables, etc., is detected by incinerating the substance, treating the ash with nitric acid and taking to dryness, the residue is taken up with water and the mixture filtered. To the filtrate is added a few cc. of 40% ammonium persulphate and a little 2% silver nitrate solution. A pink color is produced in presence of manganese.

Manganese compounds heated with borax in the oxidizing flame produce an amethyst red color. The color is destroyed in the reducing flame.

Fused with sodium carbonate and nitrate on a platinum foil manganese compounds produce a green-colored fusion ("robin egg blue").

ESTIMATION

Manganese may be determined accurately gravimetrically or volumetrically. The former methods may be used for high-grade manganese ores, the latter are generally preferred for determining manganese in steel and in alloys and are applicable to a wide range of substances.

The most important ore of manganese is pyrolusite, MnO_2. Other ores are braunite, Mn_2O_3; hausmannite, Mn_3O_4; manganite, $Mn_2O_3 \cdot H_2O$; albanite, MnS; haurite, MnS_2; dialogite, $MnCO_3$; rhodonite, $MnSiO_3$.

Speigeleisen or ferromanganese is an important alloy for the steel industry. In addition to the requirement of the element in the analysis of the above substances it is determined in certain paint pigments—green and violet manganous oxides, in dryers of oils, etc. It occurs in a number of alloys.

[1] Van Nostrand's Chem. Annual—Olsen.
[2] Circular 35 (2d Ed.) U. S. Bureau of Standards.

Preparation and Solution of the Sample

In dissolving the sample the following facts will be recalled: The metal dissolves in dilute acids, forming manganese salts. The oxides and hydroxides of manganese are soluble in hot hydrochloric acid. Manganous oxide is soluble in nitric or in sulphuric acid; the dioxide is insoluble in dilute or concentrated nitric acid, but is soluble in hot concentrated sulphuric acid.

Ores of Manganese. A sample of powdered ore weighing 1 gram is brought into solution by digesting with 25 to 50 cc. of strong hydrochloric acid for fifteen to thirty minutes on the steam bath. If much silica is present 5 to 10 cc. hydrofluoric acid will assist solution. Five cc. of sulphuric acid are added and the mixture evaporated and heated until fumes of sulphur trioxide are evolved. The residue is taken up with a little water and warmed until the sulphates have dissolved. If decomposition is incomplete and a colored residue remains, this is filtered off, ignited in a platinum dish and fused with a little potassium bisulphate. The fusion is dissolved in water containing a little nitric acid and the solution added to the bulk of the sample.

If manganese is to be determined volumetrically the removal of iron is not necessary. If, however, a gravimetric procedure is to be followed, iron and alumina are removed by the basic acetate method given under separations and manganese precipitated in the filtrate. In presence of small amounts of iron and alumina, precipitation with ammonia in presence of ammonium chloride will remove these elements without appreciable loss of manganese, a double precipitation being usually advisable. For volumetric procedures in ores containing over 2% manganese an aliquot portion of the sample is taken for the determination. The portion should not contain over 0.01 gram of manganese.

Sulphide Ores—Pyrites, etc. The sample is either roasted to oxidize the sulphide and then dissolved in hydrochloric acid as above stated or it is treated according to the procedure given for iron pyrites under sulphur.

Slags. These may be decomposed with hydrofluoric and hydrochloric acid with final expulsion of these acids with sulphuric acid. Manganese is best determined in the extract by a volumetric method.

Iron Ores. The treatment is the same as that recommended for ores of manganese. The residue remaining upon evaporation with sulphuric acid is dissolved in a little water and about 30 cc. of nitric acid (sp.gr. 1.135) added. Manganese is now determined by the bismuthate method.

Alloys. Manganese Alloys. One gram of ferromanganese is dissolved in 50 cc. of dilute nitric acid (sp.gr. 1.135) and oxidized with sodium bismuthate with boiling. The cooled solution is diluted to 500 cc. and 10 to 25 cc. is treated with about 30 cc. of dilute nitric acid and manganese determined by the bismuthate method. The amount of sample taken is governed by the manganese content. This should not exceed 0.01 gram of the element if the volumetric procedure is to be followed.

Manganese Bronze. Five grams of drillings are dissolved in dilute nitric acid (1.2), in a large beaker, using only sufficient acid to cause solution. If much free acid is present evaporation to small volume is necessary to expel the nitric acid. The concentrate is diluted to 200 cc. and hydrogen sulphide passed in to precipitate copper. The solution is diluted to 250 cc. and 50 cc. filtered off (= 1 gram). The H_2S gas is expelled by boiling, the solution being concentrated to about 15 cc. Twenty-five cc. of nitric acid are added and manganese precipitated

by adding potassium chlorate in small portions. The chlorine is boiled off and the precipitate filtered onto asbestos and washed with concentrated nitric acid. This is now determined volumetrically by treating with an excess of ferrous sulphate of known strength and titrating the excess with standard permanganate.

Ferro-titanium Alloy. This is best decomposed by fusion with sodium carbonate, to which a pinch of sodium peroxide has been added. The fusion is extracted with water and the residue containing iron, manganese and nickel filtered onto asbestos. Manganese is dissolved in 25 to 30 cc. of nitric acid by treating with SO_2 gas or hydrogen peroxide and manganese determined by the bismuthate method.

Ferro-chromium, Metallic Chromium. These are best decomposed by fusion with sodium peroxide (five times the weight of sample taken), the fusion being made in a nickel crucible. The treatment is now the same as that recommended for ferro-titanium.

Ferro-aluminum, Vanadium Alloys. The method used for steel is suitable to either of these substances.

Molybdenum Alloys. The alloy is decomposed with hydrochloric acid, and iron separated by the basic acetate method, a large excess of acetate being used. Manganese is precipitated as the dioxide by means of bromine and ammonia by the detailed procedure given later. Manganese is dissolved in nitric acid after reduction in the acid solution by addition of a little sodium thiosulphate or SO_2 gas. It is now oxidized to permanganate by means of red lead and determined either colorimetrically or by titration with a standard solution of sodium arsenite.

Tungsten Alloys. These are best decomposed by treating 1 gram of the substance with 5 to 10 cc. of hydrofluoric acid and a few cc. of strong nitric acid and digesting until the solution is complete. The hydrofluoric acid is expelled [1] by taking to dryness, a few drops of sulphuric acid having been added. The residue is taken up with water and boiled with SO_2 water. The solution is made to definite volume and manganese determined volumetrically on an aliquot portion.

Silicon Alloys. One gram of the alloy is treated with 50 cc. of dilute nitric acid (sp.gr. 1.2) and 5 cc. of hydrofluoric acid. The graphite is filtered off and the hot solution treated with sodium bismuthate and kept boiling for about fifteen minutes after the manganese dioxide has been precipitated. The bismuthate method for estimating manganese is recommended.

Iron and Steel. 0.5 to 1 gram of steel is dissolved by heating with 30 to 50 cc. of dilute nitric acid (1.135). The volumetric method by oxidation with sodium bismuthate is generally recommended, no separations of other substances being required, as manganese may be determined directly in the sample.

Pig Iron. One gram of the drillings is dissolved in 30 cc. of dilute nitric acid (1.135 sp.gr.), and as soon as the action has ceased the sample is filtered through a 7-cm. filter and the residue washed with 30 cc. more of the acid. The filtrate containing the manganese is now treated according to the procedure for steel.

[1] Brearly and Ibbotson state that although neither tungsten nor hydrofluoric acid interfere with the bismuthate method of determining manganese, the two combined lead to erratic results, hence the removal of hydrofluoric acid is necessary.

SEPARATIONS

This section includes methods of special separations of manganese from elements that may interfere in its determination. As is frequently the case, isolation of manganese is not necessary, since it may be determined volumetrically in presence of a number of elements, which would interfere in its gravimetric determination. The analyst should be sufficiently familiar with the material to avoid needless manipulations, which not only waste time, but frequently lead to inaccurate results.

Removal of Elements of the Hydrogen Sulphide Group. This separation may be required in the analysis of certain alloys where a separation of manganese from copper is required.

The acid solution containing about 4% of free hydrochloric acid (sp.gr. 1.2), is saturated with hydrogen sulphide and the sulphides filtered off. Manganese passes into the filtrate. This treatment will effect a separation of manganese from mercury, lead, bismuth, cadmium, copper, arsenic, antimony, tin and the less common elements of the group.

Separation of Manganese from the Alkaline Earths and the Alkalies. The separation is occasionally required in the analysis of clays, limestone, dolomite, etc. It is required in the complete analysis of ores. In the usual course of a complete analysis of a substance, the filtrate from the hydrogen sulphide group is boiled free of H_2S and is treated with a few cc. of nitric acid to oxidize the iron. The solution is made slightly ammoniacal with ammonia, in presence of ammonium chloride, whereby iron, aluminum and chromium are precipitated as hydroxides. The filtrate is treated with hydrogen sulphide or colorless ammonium sulphide, whereby manganese, nickel, cobalt and zinc are thrown out as sulphides and the alkaline earths and alkalies remain in solution.

Separation of Manganese from Nickel and Cobalt

The free acid of the sulphate or chloride solution of the elements is neutralized with sodium carbonate and a slight excess added. It is now made strongly acid with acetic acid and 5 grams of ammonium acetate added for every gram of nickel and cobalt present. The solution is now diluted to about 200 cc. and saturated with hydrogen sulphide, whereby nickel and cobalt are precipitated as sulphides and manganese remains in solution.

Separation of Manganese from Iron and Aluminum, Basic Acetate Method

The procedure effects a separation of iron, aluminum, titanium, zirconium and vanadium from manganese, zinc, cobalt and nickel.

The separation depends upon the fact that solutions of acetates of iron, aluminum, titanium, zirconium and vanadium are decomposed when heated and the insoluble basic acetates precipitated, whereas the acetates of manganese, zinc, cobalt and nickel remain undecomposed when boiled for a short time.

$$Fe(C_2H_3O_2)_3 + 2HOH = 2HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2.$$

The solvent action of the liberated acetic acid is prevented by the addition of sodium acetate [1] which checks ionization of the acid. The method requires care and is somewhat tedious, but the results attained are excellent.

Procedure. To the cooled acid solution of the chlorides is added a concentrated aqueous solution of sodium carbonate from a burette with constant stirring until the precipitate that forms dissolves slowly. A dilute solution of the carbonate is now added until a slight permanent opalescence is obtained. With the weak reagent and careful addition of the carbonate drop by drop the proper neutralization of the free acid is obtained. With considerable iron present the solution appears a dark red color, fading to colorless as the quantity of iron decreases to a mere trace in the solution. Three cc. of acetic acid (sp.gr. 1.044) are added to dissolve the slight precipitate. The more perfect the neutralization before heating the less amount of reagent required for precipitating iron—an excess of reagent does no harm. If this does not clear the solution in two minutes, more acetic acid is added a drop at a time until the solution clears, allowing a minute or so for the reaction to take place with each addition. The solution is diluted to about 500 cc. and heated to boiling and 6 cc. of a 30% sodium acetate solution added. The solution is boiled for one minute and removed from the flame. (Longer boiling will form a gelatinous precipitate, difficult to wash and filter.) The precipitate is allowed to settle for a minute or so, then filtered, while the liquid is hot, through a rapid filter and washed with hot, 5% sodium acetate solution three times. The apex of the filter is punctured with a glass stirring rod and the precipitate washed into the original beaker in which the precipitation was made with a fine stream of hot, 1 : 1 hydrochloric acid solution from a wash bottle. (Dilute HNO_3 may be used in place of HCl.)

A second precipitation with neutralization of the acid and addition of sodium acetate is made exactly as directed above. It is advisable to evaporate the solution to small volume to expel most of the free mineral acid before addition of Na_2CO_3 to avoid large quantities of this reagent. The filtrates contain manganese, zinc, cobalt and nickel; the precipitate iron. aluminum, titanium, zirconium, vanadium.

Separation of Manganese as the Dioxide, MnO_2

The procedure is of special value in the complete analysis of ores where a basic acetate separation of iron and aluminum has been made, and a gravimetric estimation of other constituents in the solution are desired.

The procedure depends upon the principle that manganese in a dilute solution of manganous salt is oxidized to manganese dioxide and so precipitated, when boiled with bromine or certain other oxidizing agents:

$$MnCl_2 + Br_2 + 2H_2O = MnO_2 + 2HCl + 2HBr.$$

The free acid formed by the reaction must be neutralized either by ammonia or by the presence of a salt of a weak acid such as sodium acetate, otherwise the precipitation of manganese will be incomplete. In presence of ammonium salts much of the bromine is used up in oxidizing ammonia,

$$MnCl_2 + 3NH_4OH + 2Br = MnO(OH)_2 + NH_4Br + 2NH_4Cl + HBr$$

Sodium acetate is preferred to ammonium acetate, though the latter may be used.

At the same time an acid is formed, which reacts with the free ammonia. It is necessary to have the solution ammoniacal throughout the reaction to prevent resolution of the manganese.

Procedure. To the solution containing manganese is added 4 to 5 grams of sodium acetate (unless already present in excess), the solution being diluted to about 200 cc. Bromine water is added until a distinct color of bromine is evident. The mixture is boiled and kept boiling for ten to fifteen minutes, additional bromine being added in small portions. The precipitate is allowed to settle and filtered off. The filtrate is boiled with additional bromine to ascertain whether the manganese has been completely removed from the solution.

If ammonia is present, as is frequently the case, it is advisable to add more of the reagent from time to time, the solution having a distinct odor of ammonia after the last portion of bromine has been added. When large amounts of manganese are present, several separations may be required to remove the element from the subsequent filtrates.

The precipitated dioxide may be dissolved in sulphuric acid and manganese determined volumetrically or gravimetrically.

It may be ignited directly and weighed as Mn_3O_4.

It may be evaporated with sulphuric acid and manganese determined as $MnSO_4$.

Manganates of zinc or calcium will be precipitated if present in large amounts.

Manganese may also be precipitated by ammonium persulphate in an ammoniacal solution, potassium chlorate and chloride of lime in presence of zinc chloride in a neutral solution.[1]

GRAVIMETRIC METHOD

Determination of Manganese as Pyrophosphate

Manganese is precipitated as ammonium manganese phosphate, NH_4MnPO_4, and then ignited to pyrophosphate, $Mg_2P_2O_7$. The method is known as Gibbs' Phosphate Process.[2]

Procedure. The cold solution of manganese chloride[3] obtained as directed in previous sections, should be diluted so as to contain not over 0.1 gram of manganese oxide equivalent per 100 cc. of solution. A cold saturated solution of ammonium sodium phosphate (microcosmic salt, 170 grams per liter; 9 cc. precipitates an equivalent of 0.1 gram of the oxide) is now added in slight excess. The solution is made strongly ammoniacal and heated to boiling, the boiling being continued until the precipitate becomes crystalline. After allowing to settle until cold, the precipitate is filtered off (the filtrate being tested with more of the precipitating reagent to assure that an excess had been added), and dissolved in a little dilute hydrochloric or sulphuric acid.

Reprecipitation of the phosphate. The free acid is neutralized with ammonia added in slight excess until the odor is quite distinct, the solution heated to boiling, and a few cc. of additional phosphate reagent added. The crystalline

[1] J. Pattinson's Method, Jour. Chem. Soc., **35**, 365, 1899.

[2] Gibbs' C.N., **17**, 195, 1868.

[3] Some analysts prefer to add the phosphate reagent to the strongly ammoniacal solution, boiling hot.

precipitate is filtered into a weighed Gooch crucible, washed free of chlorides with very dilute ammonia ($AgNO_3+HNO_3$ test), dried and ignited to the pyrophosphate. The ignition is conducted, as in case of magnesium, by heating first over a low flame and gradually increasing the heat to the full power of the burner. The final residue will appear white or a pale pink.

$$Mn_2P_2O_7 \times 0.4996 = MnO,$$

$$Mn_2P_2O_7 \times 0.3869 = Mn.$$

NOTES. Zinc, nickel, copper and other elements precipitated as phosphates should be absent from the solution. The separation from iron is generally made by the basic acetate method and manganese precipitated from the filtrate, free of other elements, as the peroxide MnO_2, by means of bromine added to the ammoniacal solution. Other oxidizing reagents may be used, as has been stated. The dioxide is dissolved in strong hydrochloric acid and the above precipitation effected.

VOLUMETRIC METHODS

Bismuthate Method for Determination of Manganese [1]

The method is based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of 1.135 sp.gr., when the solution is cold, but in hot solutions the excess of the bismuth tetroxide is rapidly decomposed, and then the nitric acid reacts with the permanganic acid, and, as soon as a small amount of manganous salt is formed, the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt may be filtered off, and to the clear filtrate an excess of ferrous sulphate added, and the amount necessary to deoxidize the permanganic acid determined by titrating with permanganate. The end reactions are very sharp and the method is extremely accurate, but the presence of even traces of hydrochloric acid utterly vitiates the results. As pointed out by Reddrop and Ramage, bismuth tetroxide, which was used by Schneider, is difficult to obtain free from chlorides, and they recommended **sodium bismuthate**, which they prepare as follows: Heat 20 parts of caustic soda nearly to redness in an iron or nickel crucible, and add, in small quantities at a time, 10 parts of basic bismuth nitrate, previously dried in a water oven. Then add 2 parts of sodium peroxide and pour the brownish-yellow fused mass on an iron plate to cool; when cold, break it up in a mortar, extract with water, and collect on an asbestos filter. The residue, after being washed four or five times by decantation, is dried in the water oven, then broken up and passed through a fine sieve.

Nitric acid (sp.gr. 1.135). A mixture of 3 parts of water and 1 part of strong nitric acid.

Nitric acid (3%). Thirty cc. of strong acid to the liter.

Permanganate Solution and Ferrous Sulphate Solution. One gram of potassium permanganate to the liter gives a solution of convenient strength, and 12.4 grams of ferrous ammonium sulphate and 50 cc. of strong sulphuric acid,

[1] A. A. Blair, "Chemical Analysis of Iron," J. B. Lippincott Co., Pub.

made up to 1 liter, gives a solution which is almost exactly equal to the permanganate solution. As the strength of the ferrous sulphate solution changes quite rapidly while the permanganate remains unaltered for months, it is unnecessary and troublesome to keep them of the same strength. By using a constant volume of the ferrous sulphate solution and testing it against the permanganate solution every day, the calculation of the results is very simple. It is necessary that the conditions should be the same in getting the strength of the ferrous solution as in titrating a solution for manganese, and after many experiments the following method was adopted: Measure into a 200-cc. flask 50 cc. of nitric acid (1.135), cool, and add a very small amount of bismuthate, dilute with 50 cc. of 3% nitric acid, filter into a 300-cc. flask, and wash with 50 cc. of 3% nitric acid. If the felt is well coated with bismuthate it is unnecessary to add any to the nitric acid in the flask, as filtration through the mass of bismuthate on the felt will answer the purpose. Run in from the pipette (see Fig. 46) 25 cc. of ferrous sulphate solution and titrate with the permanganate to a faint pink. This gives the value in permanganate of the ferrous sulphate solution.

The permanganate solution may be standardized in three ways:

First, by getting its value in iron, in the usual way, and calculating its value in manganese. The proportion is 5Fe : Mn or 279.2 : 54.93 = 0.1967.

Second, by titrating a steel containing a known amount of manganese and getting the value of the solution by dividing the percentage of manganese by the number of cc. of the permanganate used.

Third, by making a solution of pure manganese sulphate and determining the manganese in it by evaporating a weighed amount of the solution to dryness, heating to dull redness, and weighing as manganese sulphate, which, multiplied by 0.36377, gives the amount of manganese. Five grams of C.P. manganese sulphate dissolved in 500 cc. of water and filtered will give a solution containing about 0.0035 gram of manganese to the gram of solution. Weigh 1 to 3 grams of the solution in a crucible, transfer to a 200-cc. flask, using 50 cc. of nitric acid (sp.gr. 1.135), cool, and add 0.5 to 1 gram bismuthate, and allow it to stand for three or four minutes, shaking at intervals. Add 50 cc. of 3% nitric acid and filter through the asbestos filter and wash with 50 or 60 cc. of the same acid. Run 25 cc. of the ferrous sulphate solution into the flask from the pipette and titrate with the permanganate solution to a faint pink. Subtract the number of cc. of the permanganate solution obtained from the value of the 25 cc. of the ferrous sulphate solution in permanganate, and the result is the number of cc. of the permanganate corresponding to the manganese in the manganese sulphate solution used. Divide the weight of the manganese in the manganese sulphate used by the number of cc. of permanganate and the result is the value of 1 cc. of the permanganate solution in manganese.

Example. One gram manganese sulphate solution contains 0.003562 gram manganese; 2.0372 grams manganese sulphate solution equal 0.0072565 gram manganese; 25 cc. ferrous sulphate solution equal 24.5 cc. permanganate solution; 2.0372 grams manganese sulphate solution, after oxidation and addition of 25 cc. ferrous sulphate solution, require 3.6 cc. permanganate solution; 24.5 cc. − 3.6 cc. = 20.9 cc.; 0.0072565 divided by 20.9 = 0.0003472, or 1 gram permanganate equals 0.0003472 gram manganese. If, then, 1 gram of steel, after oxidation and addition of 25 cc. ferrous sulphate solution, requires 6.2 cc. permanganate solution to give the pink color, $24.5 - 6.2 = 18.3 \times 0.0003472 = 0.006354$ gram, or the sample contains 0.635% manganese.

Procedure. The nitric acid solution of the sample placed in a 200-cc. Erlenmeyer flask is treated as follows:

Cool, and add about 0.5 gram of bismuthate. The bismuthate may be measured in a small spoon, and experience will soon enable the operator to judge of the amount with sufficient accuracy. Heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add sulphurous acid, solution of ferrous sulphate, or sodium thiosulphate, in sufficient amount to clear the solution, and heat until all nitrous oxide has been driven off. Cool to about 15° C., add an excess of bismuthate, and agitate for a few minutes. Add 50 cc. of water containing 30 cc. of nitric acid to the liter, and filter through an asbestos felt on a platinum cone into a 300-cc. Erlenmeyer flask, using suction (see Fig. 45), and wash with 50 to 100 cc. of the same acid. Run into the flask from a pipette (Fig. 46) a measured volume of ferrous sulphate solution and titrate to a faint pink color with permanganate. The number of cc. of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous sulphate used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the permanganate in manganese, gives the amount of manganese in the sample.

FIG. 45.

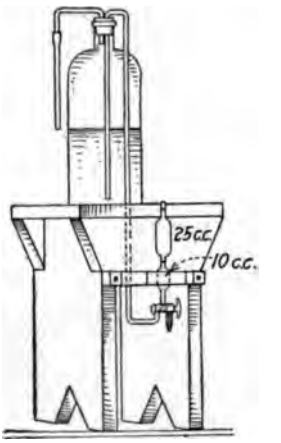


FIG. 46.

NOTE. In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if not, another treatment with bismuthate is necessary.

Notes and Precautions

Special Steels.. Steels containing chronium offer no special difficulties, except that it must be noted that while in hot solutions the chromium is oxidized to chromic acid, which is reduced by the addition of sulphurous acid, the oxidation proceeds so slowly in cold solutions that if there is no delay in the filtration and titration the results are not affected. Steels containing tungsten are sometimes troublesome on account of the necessity for getting rid of the tungstic acid. Those that decompose readily in nitric acid may be filtered and the filtrate treated like pig iron, but when it is necessary to use hydrochloric acid it is best to treat with aqua regia, evaporate to dryness, redissolve in hydrochloric acid, add a few drops of nitric acid, dilute, boil, and filter. Get rid of every trace of hydrochloric acid by repeated evaporations with nitric acid, and proceed as with an ordinary steel.

The delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is extraordinary; 0.000005 gram of manganese gave an appreciable color in 50 cc. of solution.

As will be seen in the description of the various methods of solution, the use of hydrochloric acid has been avoided, because the presence of even traces of this reagent is fatal to the accuracy of the method. Where it is impossible to avoid its use, and its presence is suspected in the final nitric acid solution, the addition of a

drop or two of silver nitrate will overcome the difficulty, but the filter must be rejected after using it for filtering a solution so treated.

Any form of asbestos filtering tube may be used for filtering off bismuthate, but the perforated cone with bell jar is the most satisfactory, because it has the largest area of filtering service. One filter may be used for fifty or more determinations, and the time occupied in filtering and washing one determination is only from one minute and a half to three minutes. The filtrate must be clear, for the least particle of bismuthate carried through will vitiate the result by reacting with the excess of ferrous sulphate. As soon as the filtration and washing are completed, the ferrous sulphate should be added, and the excess titrated with the permanganate solution, as the permanganic acid gradually decomposes on standing, and the warmer the solution the more rapid is the decomposition. At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C., fifteen minutes will show an appreciable change. The larger the amount of manganese the more rapid the change.

It is especially important not to allow the solution to stand after adding the ferrous sulphate, as the excess of this reagent reacts with the nitric acid in a few minutes and the formation of the smallest amount of nitrous oxide is fatal to the accuracy of the determination. For this reason it is important to boil off every trace of nitrous oxide when, in the earlier part of the operation, sulphurous acid or other deoxidizing agent is added.

When working with steels of unknown manganese content, it may often happen that 25 cc. of ferrous sulphate solution are insufficient to entirely reduce the permanganic acid, in which case an additional amount of ferrous sulphate must be added. It will be noticed that the solution of permanganic acid upon the addition of an insufficient amount of ferrous sulphate does not necessarily retain its pink or purple color, but usually changes to a dirty brown. When this occurs 10 cc. more of ferrous sulphate is added to the flask and the value of the two additions taken as the amount from which the number of cc. of permanganate, corresponding to the excess of ferrous sulphate, must be subtracted. When the sample is low in manganese, the 10 cc. ferrous sulphate alone may be used.

These is no advantage in using permanganate solutions differing in strength from the one given above, but the strength of the ferrous sulphate solution may be changed to meet special cases.

Volhard's Method for Manganese[1]

The method is based on the principle that when potassium permanganate is added to a neutral manganese salt all of the manganese is oxidized and precipitated. When this stage is reached any excess of permanganate is immediately evident by the color produced. The calculation of results may be based on the reaction,

$$3MnSO_4+2KMnO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4,$$

or

$$5ZnSO_4+6MnSO_4+4KMnO_4+14H_2O=4KHSO_4+7H_2SO_4+5ZnH_2\cdot 2MnO_3,$$

the ratio in either case being $2KMnO_4=3Mn$.

Procedure. The material decomposed with hydrochloric and nitric acid and taken to fumes with sulphuric acid, as stated for the preparation of the sample, is cooled and boiled with 25 cc. of water until the anhydrous ferric sulphate has dissolved and continue as follows: Transfer the mixture to a 500-cc. graduated flask and add an emulsion of zinc oxide in slight excess to precipitate the iron (C.P. $ZnSO_4$ precipitated by KOH added to slight alkalinity. The washed precipitate is kept in a stoppered bottle with sufficient water to form an emulsion).

[1] A. H. Low, "Technical Methods of Ore Analysis," 7th Ed., John Wiley & Sons, Pub. (See procedure for Analysis of Spiegel Iron.)

Agitate the flask to facilitate the precipitation and see that a slight excess of zinc oxide remains when the reaction is complete. Now dilute the contents of the flask up to the mark with cold water, mix thoroughly and allow to stand a short time and partially settle. By means of a graduated pipette draw off 100 cc. of the clear supernatant liquid and transfer it to an 8-oz. flask. While the precipitate in the 500-cc. flask may appear large, it actually occupies but a very small space, and any error caused by it may consequently be neglected. Likewise the error in measurement due to change of temperature during the manipulation is insignificant. Heat the solution in the small flask to boiling, add two or three drops of nitric acid (which causes the subsequent precipitate to settle more quickly) and titrate with a standard solution of potassium permanganate. The permanganate causes a precipitate which clouds the liquid and it is therefore necessary to titrate cautiously and agitate the flask after each addition, and then allow the precipitate to settle sufficiently to observe whether or not the solution is colored pink. A little experience will enable one to judge by the volume of the precipitate formed, about how rapidly to run in the permanganate. The final pink tinge, indicating the end of the reaction, is best observed by holding the flask against a white background and observing the upper edges of the liquid. When this point is attained, bring the contents of the flask nearly to a boil once more and again observe if the pink tint still persists, adding more permanganate if necessary. In making this end-test avoid actually boiling the liquid, as a continual destruction of the color may sometimes thus be effected and the true end-point considerably passed. When the color thus remains permanent the operation is ended. Observe the number of cc. of permanganate solution used and calculate the result.

It is customary to use the same permanganate solution for both iron and manganese. Having determined the factor for iron, this may be multiplied by 0.2952 to obtain the factor for manganese. It will be observed that $2KMnO_4$ are required for 3Mn, and in the reaction for iron that $2KMnO_4$ are required for 10Fe. Therefore 558.4 parts of iron are equivalent to 164.79 parts of manganese, or, 1 part of iron to 0.2951 part of manganese.

$$3MnSO_4+2KMnO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4,$$

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

Ammonium Persulphate Method for Determining Small Amounts of Manganese by Colorimetric Comparison or by Titration

The process depends upon the oxidation of manganous salts to permanganate by ammonium persulphate in presence of a catalytic agent such as silver nitrate:

$$2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O=5(NH_4)_2SO_4+5H_2SO_4+4HNO_3+2HMnO_4.$$

The reaction takes place equally well in sulphuric or in nitric acid solution, or in a mixture of the two. The essential point is the presence of a sufficient amount of silver nitrate catalyst.

Procedure. One gram of ore is dissolved in hydrochloric acid, followed by sulphuric and taken to fumes as directed under Preparation and Solution of the Sample. The sulphate taken up with water is made to a volume of 100 cc. If the color comparison is to be made the solution should be filtered through a dry filter, otherwise the filtration may be omitted. Twenty cc. (equal to 0.2

gram) of the material is taken for the test. In the case of steel, 0.1 to 0.2 gram of the drilling, dissolved in dilute nitric acid, is taken.

Oxidation. The solution is transferred to a test-tube, 1×10 ins., if the color comparison is to be made, or into a 150-cc. Erlenmeyer flask, if the sample is to be titrated. Fifteen cc. of silver nitrate solution (1.5 grams $AgNO_3$ per liter of water), are added; the solution heated to 80 to 90° C. by placing the receptacle in hot water, and then 1 gram of ammonium persulphate added. When the color commences to develop the sample is cooled in cold water, while the evolution of oxygen continues. The sample is poured into the comparison tube and the color compared with that obtained from an ore or steel sample of known manganese content, run in the same way.

In the titration method the solution in the Erlenmeyer flask is diluted to about 100 cc., 10 cc. of 0.2% salt solution added, and the sample titrated with standard sodium arsenite until the permanganate color is destroyed. The cc. of the reagent used multiplied by the factor per cc. in terms of manganese equals weight of manganese in the sample titrated.

NOTE. Arsenious acid reagent is made by dissolving 10 grams of arsenious oxide in water containing 30 grams of sodium carbonate. The solution is diluted to 1 liter. 125 cc. of this solution are diluted to 2000 cc. This latter reagent is standardized against an ore or sample of steel of known manganese content, following the directions given under the procedure outlined.

Oxidation of Manganese to Permanganate by Red Lead

Red lead oxidizes manganese in nitric acid solution to permanganate. The method is suitable for determining this element in steel and iron in presence of molybdenum, aluminum, tungsten, copper and nickel, in amounts such as are apt to be present. The method is given in the chapter on Iron in the Analysis of Iron and Steel, page 227.

ANALYSIS OF SPIEGEL IRON FOR MANGANESE[1]

Procedure. Weigh 0.5 gram of the sample in a 250-cc. beaker, add 40 cc. dilute HNO_3 (1-2), cover with a watch-crystal, heat over Bunsen burner and finally expel nitrous fumes by boiling down to a small volume (5 cc.).[2] Wash into a 500-cc. graduated flask, fill about half full, neutralize with an emulsion of zinc oxide, adding enough to precipitate the iron and a *slight* excess.[3] Dilute to the mark, shake well, pour into a 600-cc. beaker and mix by pouring back into the flask and then into beaker. Allow the precipitate to settle, decant off two 100-cc. portions of clear solution into 350-cc. casseroles. Add 100 cc. water, heat to boiling and titrate with standard $KMnO_4$, stirring thoroughly with heavy glass rod. Run in about 1 cc. at a time until the end-point is passed.[4] Titrate the second portion, running it up to within 1 cc. of the end-point, and finishing a drop or two at a time, stirring thoroughly between each addition.[5] The burette reading gives percentage of Mn directly.

[1] Procedure communicated to the author by Dr. Breyer.

[2] It is necessary to boil off nitrous fumes, as they will consume $KMnO_4$.

[3] Always test the zinc oxide for reducing substances.

[4] In samples in which the percentage of Mn is known approximately, almost the full amount of $KMnO_4$ can be added at once.

[5] Do not mistake the reflection of precipitated MnO_2 for excess of $KMnO_4$. If properly carried out the MnO_2 should collect in center of casserole.

Preparation and Standardization of Permanganate.[1] Dissolve 23.23 grams C.P. $KMnO_4$ in 12 liters of distilled water, shake thoroughly and allow to stand a week or two before using.

Standardization. Weigh .15 gram C.P. sodium oxalate (Bureau of Standards) into a 400-cc. beaker. Dissolve in 200 to 250 cc. hot water (80 to 90°), add 10 cc. (1 : 1) sulphuric acid. Titrate at once with $KMnO_4$, until 1 drop gives a permanent pink.

When .15 gram sodium oxalate is taken, it should consume 36.87 cc. $KMnO_4$, if the permanganate is of correct strength, i.e., 1 cc. = 1% in .1 gram sample titrated.

[1] The Standardization of $KMnO_4$ solution by Sodium Oxalate, McBride, J.A.C.S., **34**, 393. Miller, "Quantitative Analysis for Mining Engineers."

MERCURY

WILFRED W. SCOTT

Hg, *at.wt.* 200.6; *sp.gr.* 13.595;[1] *m.p.* 38.90°;[2] *b.p.* 357.33° C;[1] *oxides*, Hg_2O, HgO.

DETECTION

Metallic mercury is recognized by its physical properties. It is the only metal which is a liquid at ordinary temperatures. The element forms a convex surface when placed on glass.

Mercury in the mercurous form is precipitated by hydrochloric acid as white mercurous chloride, HgCl. This compound is changed by ammonium hydroxide to the black precipitate of metallic mercury and nitrogen dihydrogen mercuric chloride.[3]

Mercury in the mercuric form is not precipitated by hydrochloric acid. The sulphide of the element is thrown out from an acid solution as black HgS. The precipitate first appears white, changing to orange-yellow, then brown and finally to black, as the H_2S gas is passed into the solution. The element is distinguished from the other members of the group by the insolubility of its sulphide in yellow ammonium sulphide and in dilute nitric acid.

If the mercury sulphide is dissolved in aqua regia, the nitric acid expelled by taking to dryness, then adding hydrochloric acid and evaporating again to dryness, the residue taken up with a little hydrochloric acid, diluted with water, and treated with a solution of stannous chloride, a white precipitate of mercurous chloride is first formed, which is further reduced to metallic mercury by an excess of the reagent.

ESTIMATION

The metal is found free in the upper portions of cinnabar deposits. As an amalgam with silver it occurs in horn silver. Cinnabar, HgS, is the only ore of mercury of commercial importance. The element has been found in quartz, sandstone, schists, iron pyrites, bituminous substances, eruptive and sedimentary rocks of all ages. It occurs in sulphide ores of other metals—especially in zinc ores.

Preparation and Solution of the Sample

It will be recalled that nitric acid is the best solvent for the metal and its amalgams. The oxides are insoluble in alkalies. Mercuric oxide is dissolved by acids. Hydrochloric acid forms mercurous chloride with the lower oxide, insoluble in dilute hydrochloric acid.

[1] Van Nostrand's Chem. Annual—Olsen.
[2] Circular 35 (2d Ed.) U. S. Bureau of Standards.
[3] Prescott and Johnson, "Qualitative Chemical Analysis."

Ores. If mercury is to be determined by the dry procedure, the finely ground sample may be mixed directly with the flux and determined as directed later.

For the wet methods the ore is decomposed in a covered porcelain dish with **aqua regia,** heating gently. The solution is evaporated to dryness on the water bath. The residue is taken up with hydrochloric acid and again evaporated to dryness to expel the nitric acid. The residue is again dissolved by adding a little hydrochloric acid. Mercury will now be in solution and may be determined by precipitation as mercuric sulphide by the gravimetric procedure.

For opening up the ore for the volumetric method by Seamon see method at close of the chapter, page 274.

SEPARATIONS

Separation of Mercury from the Iron and Zinc Groups, or from the Alkaline Earths and the Alkalies. Mercury is precipitated as a sulphide from an acid solution of the mercuric salt by hydrogen sulphide, together with the members of the hydrogen sulphide group. Sufficient acid should be present to prevent the precipitation of zinc sulphide. Iron, aluminum, chromium, manganese, cobalt, nickel, zinc, the alkaline earths and the alkalies remain in solution.

Separation of Mercury from Arsenic, Antimony, and Tin. The sulphides obtained by passing hydrogen sulphide into an acid solution, preferably of the chlorides, are digested with yellow ammonium sulphide solution. Arsenic, antimony and tin dissolve, whereas mercury sulphide remains insoluble. Sulphides of the fixed alkalies dissolve mercury as well as arsenic, antimony and tin, so cannot be used in effecting a separation.

Separation from Lead, Bismuth, Copper and Cadmium. These elements remain with mercury upon removal of arsenic, antimony and tin as their sulphides are insoluble in ammonium sulphide. (CuS slightly soluble.) The precipitated sulphides are transferred to a porcelain dish and boiled with dilute nitric acid, sp.gr. 1.2 to 1.3. After diluting slightly with water the solution is filtered and the residue of mercuric sulphide washed with dilute nitric acid and finally with water. If much lead is present in the solution it is apt to contaminate the residue by a portion being oxidized to lead sulphate and remaining insoluble. In this case the residue is treated with aqua regia, the solution diluted and mercury chloride filtered from $PbSO_4$ and free sulphur. Mercury is best determined as HgS by the ammonium sulphide method described later. Traces of lead do not interfere, as lead is completely removed by remaining insoluble in potassium hydroxide, whereas mercury sulphide dissolves. See method.

Separation from Selenium and Tellurium. The mercury selenide or telluride is dissolved in aqua regia, chlorine water added and the solution diluted to 600 to 800 cc., phosphorous acid is added and the solution allowed to stand for some time; mercurous chloride is precipitated, selenium and tellurium remaining in solution. Selenium and tellurium will precipitate in hot concentrated solutions when treated with phosphorous acid, but not in dilute hydrochloric acid solutions.

Mercury in Organic Substances. The material is decomposed by heating in a closed tube with concentrated nitric acid. Mercury is now precipitated as a sulphide with ammonium sulphide as directed in the procedure given later.

GRAVIMETRIC METHODS

Determination of Mercury by Precipitation with Ammonium Sulphide

The following method, suggested by Volhard, is generally applicable for determination of mercury. The element is precipitated by ammonium sulphide as HgS. The precipitate dissolved in caustic is again thrown out by addition of ammonium nitrate to the sulpho salt solution of mercury.

$$Hg(SNa)_2 + 2NH_4NO_3 = 2NaNO_3 + (NH_4)_2S + HgS.$$

Procedure. The acid solution of the mercuric salt is nearly neutralized by pure sodium carbonate, and is then heated with a slight excess of freshly prepared ammonium sulphide. Pure sodium hydroxide solution is added until the dark-colored liquid begins to lighten. The solution is now heated to boiling and more sodium hydroxide added until the liquid is clear. If lead is present it will remain undissolved and should be filtered off. Ammonium nitrate is now added to the solution in excess and the mixture boiled until the greater part of the ammonia has been expelled. The clear liquid is decanted from the precipitate through a weighed Gooch crucible and the precipitate washed by decantation with hot water and finally transferred to the crucible and washed two or three times more. The mercuric sulphide is dried at 110° C. and weighed as HgS.

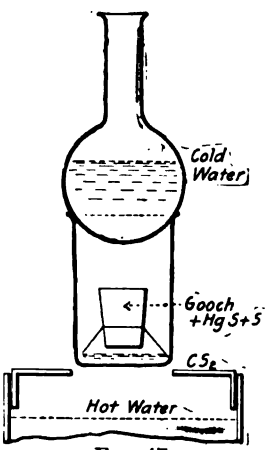


FIG. 47.

$$HgS \times 0.8622 = Hg \quad \text{or} \quad \times 0.9307 = HgO.$$

NOTES. Alumina and silica are apt to be present in caustic.

Free sulphur may be removed, if present, by boiling with sodium sulphite, $Na_2SO_3 + S = Na_2S_2O_3$. The sulphur may be extracted with carbon disulphide. The Gooch crucible is placed upon a glass tripod in a beaker, containing carbon disulphide, and a round-bottomed flask filled with cold water is placed over the mouth of the beaker to serve as a condenser, Fig. 47. By gently heating over a water bath for an hour the sulphur is completely extracted from the sulphide. Carbon disulphide is removed from the precipitate by washing once with alcohol followed by ether. The residue is now dried and weighed.

Determination of Mercury by Electrolysis

Mercury is readily deposited as a metal from slightly acid solutions of its salts.

Procedure. The neutral or slightly acid solution of mercuric or mercurous salt is diluted in a beaker to 150 cc. with water and 2 to 3 cc. of nitric acid added. The solution is electrolyzed with a current of 0.5 to 0.1 ampere, and an E.M.F. of 3.5 to 5 volts. A gauze cathode is recommended, or a platinum dish with dulled inner surface may be used. One gram of mercury may be deposited in about fifteen hours (or overnight). The time may be shortened to about three hours by increasing the current to 0.6 to 1 ampere.

The metal is washed with water without interrupting the current and then with alcohol. After removing the adhering alcohol with a filter paper, the cathode is placed in a desiccator containing fused potash and a small dish of mercury. The object of this mercury is to prevent loss of the deposit by vaporization.

The increased weight of the cathode is due to metallic mercury.

NOTES. In the electrolysis of mercuric chloride turbidity may be caused by formation of mercurous chloride by reduction, but this does no harm, as the reduction to metallic mercury follows.

Mercury may be electrolyzed from its sulpho solutions, obtained by dissolving its sulphide in concentrated sodium sulphide.

Determination of Mercury by the Holloway-Eschka Process Modified

When mercury sulphide is heated with iron filings metallic mercury is volatilized, iron sulphide being formed. The mercury vapor is condensed on a silver or gold plate. The use of iron for this reduction was suggested by Eschka and his method modified by Holloway. In ores containing arsenic the addition of zinc oxide is recommended. Erdmann and Marchand use lime for decomposing the mercury compound. The reactions may be represented as follows:

$$HgS+Fe=FeS+Hg \quad \text{or} \quad HgX+CaO=CaX+Hg+O.$$

Apparatus. This consists of a deep glazed porcelain crucible, the size depending upon the charge of the sample to be taken. Generally a 30-cc. crucible is used for a 2-gram sample with 4 grams of flux. The crucible is covered by a silver or gold plate that lies perfectly flat and fits snugly around the edges of the crucible. It may be necessary to grind the top of the receptacle on emery paper to obtain a perfectly level edge.

The crucible is suspended in a hole through an asbestos board or quartz plate, to prevent the flame heating the upper portion of the vessel.

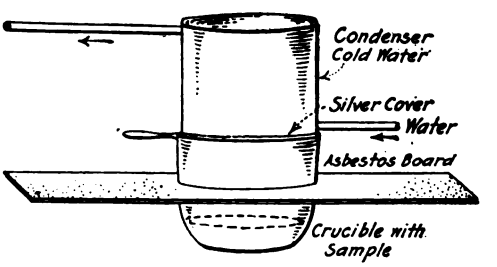


FIG. 48.

The lid of the crucible is kept cool by a cylindrical condenser of metal through which a stream of water passes. A small Erlenmeyer flask may be used, with a tube passing to the bottom of the flask through a rubber stopper, and a second tube just passing through the stopper.

Holloway has a weight placed on the metal condenser to hold the lid firmly against the crucible. The illustration (Fig. 48) shows the form of the apparatus set up for the run.

Procedure. The sample containing not over 0.1 gram of mercury is placed in the crucible with 5 to 10 grams of fine iron filings and intimately mixed. Additional filings are put over the charge. Sulphide ores containing arsenic are best mixed with about twice the weight of a flux of zinc oxide and sodium carbonate in the proportion 4 to 1, and about five times the weight of iron filings added.

The weighed silver cover is placed on the crucible and the apparatus set up as shown in the illustration, Fig. 48.

The bottom of the crucible is gradually heated with a small Méker flame until it glows slightly. Overheating should be avoided. The upper portion of the crucible should never become hot and the lid should remain cold. After heating for about thirty minutes the system is allowed to cool without disconnecting the condenser. The disk is now removed, dipped in alcohol and dried in a desiccator over fused potash or soda. The increase of weight of the dried disk is due to metallic mercury.

NOTES. If the sample contains less than 1% mercury, take 2 grams; if 1 to 2% mercury, take 1 gram; if the sample contains 2 to 5%, take 0.5-gram sample. If high in mercury, grind sample with sand and take an aliquot portion.

It is advisable to repeat the test with a clean foil to be sure that all the mercury has been driven out of the sample. The foil may be freed from mercury by heating.

VOLUMETRIC DETERMINATION OF MERCURY

Seamon's Volumetric Method [1]

Seamon's Volumetric Method.[2] Weigh 0.5 gram of the finely ground ore into an Erlenmeyer flask of 125 cc. capacity. Add 5 cc. of strong hydrochloric acid and allow it to act for about ten minutes at a temperature of about 40° C., then add 3 cc. of strong nitric acid and allow the action to continue for about ten minutes longer. The mercury should now all be in solution. Now if lead be present, add 5 cc. of strong sulphuric acid; it may be omitted otherwise. Dilute with 15 cc. of water and then add ammonia cautiously until the liquid is slightly alkaline. Bismuth, if present, will be precipitated. Acidify faintly with nitric acid, filter, receiving the filtrate in a beaker, and wash thoroughly.

Add to the filtrate 1 cc. of strong nitric acid that has been made brownish in color by exposure to the light, and titrate with a standard solution of potassium iodide until a drop of the liquid brought into contact with a drop of starch liquor, on a spot-plate, shows a faint bluish tinge. It is a good plan to set aside about one-third of the mercury solution and add it in portions until the end-point is successively passed, finally rinsing in the last portion and titrating to the end-point very carefully.

Deduct 0.5 cc. from the burette reading and multiply the remaining cc. used by the percentage value of 1 cc. in mercury to obtain the percentage in the ore.

The standard potassium iodide solution should contain 8.3 grams of the salt per liter. Standardize against pure mercuric chloride. Dissolve a weighed amount of the salt in water, add 2 cc. of the discolored nitric acid and titrate as above. One cc. of standard solution will be found equivalent to about 0.005 gram of mercury, or about 1% on the basis of 0.5 gram of ore taken for assay.

The precipitate of red mercuric iodide which forms during the titration may not appear if the amount of mercury present is very small, but this failure to precipitate does not appear to affect the result.

Iron, copper, bismuth, antimony, and arsenic, when added separately to the ore, did not influence the results in Seamon's tests. Silver interferes. Duplicate results should check within 0.1 to 0.2 of 1%.

[1] A. H. Low, "Technical Methods of Ore Analysis."
[2] "Manual for Assayers and Chemists," p. 112.

MOLYBDENUM

WILFRED W. SCOTT

Mo, *at.wt.* 96.0; *sp.gr.* 8.6–9.01; *m.p.* 2500° C; *oxides*, Mo_2O_3, MoO_2, MoO_3

DETECTION

Molybdenum appears in the hydrogen sulphide group, being precipitated by H_2S in acid solution as the sulphide. It passes into solution by digestion with ammonium sulphide or sodium sulphide along with arsenic, antimony, tin, gold and platinum. By addition of metallic zinc, antimony, together with tin, gold and platinum are precipitated as metals while molybdenum remains in solution. Arsenic, that has not volatilized as arsine, is expelled by evaporation. Nitric acid is now added and the solution taken to dryness. Molybdenum is extracted from the residue with ammonium hydroxide.

A dilute solution of ammonium molybdate treated with a soluble sulphide gives a blue solution.

Sodium thiosulphate added to a slightly acid solution of ammonium molybdate produces a blue precipitate with a supernatant blue solution. With more acid a brown precipitate is formed.

Sulphur dioxide produces a bluish-green precipitate if sufficient molybdenum is present, or a colored solution with small amounts. The reducing agents, stannous chloride, or zinc in acid solution, produce a play of colors when they react with molybdenum solutions, due to the formation of the lower oxides. The solution becomes blue, changing to green, brown and yellow.

Molybdenum present as molybdate is precipitated by *disodium phosphate* as yellow ammonium phosphomolybdate from a nitric acid solution. The precipitate is soluble in ammonium hydroxide.

A pinch of powdered mineral on a porcelain lid, moistened with a few drops of *strong sulphuric acid*, stirred and heated to fumes, then cooled, will produce a blue color when breathed upon. The color disappears on heating, but reappears on cooling. Water destroys the color.

Molybdenite is very similar to graphite in appearance. It is distinguished from it by the fact that nitric acid reacts with molybdenite, MoS_2, leaving a white residue, but has no action upon graphite. The blowpipe gives SO_2 with molybdenite and CO_2 with graphite.

ESTIMATION

The determination is required in the ores—molybdenite, MoS_2, (60% Mo); molybdite, MoO_3 (straw yellow); wulfenite, $PbMoO_4$ (yellow, bright red, olive green or colorless); Ilsemannite, MoO_3+MoO_2; powellite, $CaMoO_4$; pateraite, $CoMoO_4$; belonesite, $MgMoO_4$; eosite, lead-vanado-molybdate; achromatite,

lead molybdate and arsenate with tin oxide and lead chloride. Some iron and copper ores also contain molybdenum.

The metal is determined in certain self-hardening steels and alloys.

The reagents ammonium molybdate and the oxide-molybdic acid, MoO_3, are valuable for analytical purposes. Tests of their purity may be required.

Preparation and Solution of the Sample

In dissolving the substance the following facts should be kept in mind: The metal is easily soluble in aqua regia; soluble in hot concentrated sulphuric acid, soluble in dilute nitric acid, oxidized by excess to MoO_3. It is dissolved by fusion with sodium carbonate and potassium nitrate mixture. It is insoluble in hydrochloric, hydrofluoric and dilute sulphuric acids.

The oxide MoO_3 is but slightly soluble in acids and alkalies; MoO_2 is insoluble in hydrochloric and hydrofluoric acids. MoO_3, as ordinarily precipitated, is soluble in inorganic acids and in alkalies. The oxide sublimed is difficultly soluble.

Molybdates of the heavy metals are insoluble in water, the alkali molybdates are soluble.

Ores. Molybdenum ores are best decomposed by fusion with a mixture of sodium carbonate and potassium nitrate. The cooled fusion is then extracted with hydrochloric acid and molybdenum determined according to one of the procedures described later.

Steel and Iron. One to 2 grams of the drillings are dissolved in a mixture of hydrochloric and nitric acid (25 cc. HCl+1 cc. HNO_3), with gentle heating. Additional nitric acid is added if required or potassium chlorate may be used to oxidize the iron.

SEPARATION OF MOLYBDENUM FROM OTHER ELEMENTS

Separation from Iron. Procedure in Presence of Large Amounts of Iron. The occurrence of molybdenum with iron and its commercial importance in iron materials calls for this procedure as one commonly required in the determination of molybdenum.

The solution is nearly neutralized with a 2N. NaOH solution, added from a burette cautiously, avoiding an amount that would produce a color with iron or form a basic molybdate. If tungsten is present or if molybdic acid has precipitated in the solution or is suspected, the sample should be filtered and the residue treated as directed below. Sufficient 2N. NaOH to precipitate all the iron present in the sample (27 cc. of 2N. NaOH will precipitate 1 gram Fe) with about 40 cc. in excess is poured into a 500-cc. flask. If filtration is necessary, the paper and residue are dropped in the flask, the filter broken up, and the caustic heated to boiling to dissolve the molybdic acid. The solution containing the molybdenum is also heated to boiling and added to the hot NaOH solution, through a funnel with a constricted stem, agitating the sodium hydroxide during the addition. Iron hydroxide, $Fe(OH)_3$, is precipitated free from molybdenum, which remains in solution. The volume is made up to exactly 500 cc. and the precipitate allowed to settle; 250 cc. are filtered off and taken for the precipitation of molybdenum. Methyl orange is added as an indicator and the caustic neutralized with HCl. If barium, strontium, uranium, arsenic, cadmium and aluminum are present, 10 to 15 cc. strong hydrochloric acid are added

in excess, followed by sufficient ammonium acetate to combine with the free mineral acid.

This method, followed by the lead molybdate precipitation as given in the gravimetric methods, will effect a separation of molybdenum from barium, calcium, strontium, arsenic, cadmium, phosphorus, aluminum, uranium, manganese, cobalt, nickel, zinc, chromium, magnesium, mercury, copper as well as iron.

Separation from the Alkalies. Molybdenum, precipitated as mercurous molybdate, by adding mercurous nitrate to the slightly acetic acid solution, or as molybdenum sulphide by H_2S passed into the sulphuric acid solution, is separated from the alkalies.

If hydrogen sulphide is passed into the sulphuric acid solution, separation of molybdenum from the members of the ammonium sulphide group is effected, as well as from members of subsequent groups.

Separation from the Alkaline Earths. Fusion of the substance with sodium carbonate and extraction of the melt with water gives a solution of molybdenum, whereas the carbonates of barium, calcium and strontium remain undissolved as carbonates.

Separation from Lead, Copper, Cadmium and Bismuth. The sulphides of the elements are treated with sodium hydroxide and sodium sulphide solution and are digested by gently heating in a pressure flask. Molybdenum dissolves, whereas lead, copper, cadmium and bismuth remain insoluble. If the solution of the above elements is taken, made strongly alkaline, and treated with H_2S, the sulphides of the latter elements are precipitated and molybdenum remains in solution. The precipitates are filtered off and the filtrate containing molybdenum is placed in the pressure flask, the solution made slightly acid with sulphuric acid and the mixture heated under pressure, until the liquid appears colorless, MoS_2 is precipitated and may be converted into the oxide as described later.

Separation from vanadium is effected by a molybdenum sulphide precipitation in acid solution.

Separation from Arsenic. Arsenic, present in the higher state of oxidation, is precipitated by magnesia mixture, added to a slightly acid solution (5 cc. of concentrated hydrochloric acid per 100 cc. of solution for each 0.1 gram arsenic). The solution is neutralized with ammonia (methyl orange), and the arsenic salt filtered off. MoS_2 is now precipitated with H_2S in presence of free sulphuric acid in the pressure flask.

Separation from Phosphoric Acid. Phosphoric acid is precipitated from an ammoniacal solution as magnesium ammonium phosphate. Molybdenum may then be precipitated as the sulphide from the filtrate.

Separation from Titanium. The metals of the ammonium sulphide group are precipitated by adding ammonium hydroxide and ammonium sulphide. Molybdenum remains in solution and passes into the filtrate. H_2S is passed into the solution until it appears red; sulphuric acid is then added until the solution is acid, when molybdenum sulphide precipitates.

Separation from Tungsten. Molybdenum, precipitated with tungsten by the lead molybdate method, is ignited and the mixture then treated with hydrochloric acid and a few drops of nitric acid and evaporated nearly to dryness. Dilute hydrochloric acid is added and the solution filtered. Tungsten remains undissolved.

Molybdenum may be precipitated by H_2S as MoS_2 in presence of tartaric acid. Tungsten does not precipitate.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM

Precipitation as Lead Molybdate

Preliminary Remarks. This method, suggested by Chatard, has been pronounced by Brearly and Ibbotson to be "one of the most stable processes found in analytical chemistry." "It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulphates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. From faintly acid solution lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, manganese, zinc, magnesium and mercury salts." It may be readily separated from iron and chromium. Barium, strontium, uranium, arsenic, cadmium and aluminum do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid.

The precipitate is granular, easily filtered and washed.

Vanadium and tungsten, if present, must be removed, by separating from molybdenum by one of the procedures given.

Special Reagents. ***Lead Acetate.*** A 4% solution is made by dissolving 20 grams of the salt in 500 cc. of warm water. A few cc. of acetic acid are added to clear the solution.

Precipitation of Lead Molybdate. An excess of lead acetate is added to the acetic acid solution, containing molybdenum (see Separation in Presence of Large Amounts of Iron), (10 cc. of 4% solution of the crystallized lead acetate salt will precipitate 0.01 gram of molybdenum). The solution is heated to boiling, the crystalline precipitate allowed to settle for a few minutes on the steam bath, then filtered hot onto an ashless filter (S. & S. No. 590 quality) and washed free of chlorides with hot water.

The precipitate dried and ignited in a porcelain crucible at red heat for about twenty minutes is weighed as $PbMoO_4$.

$$PbMoO_4 \times 0.2615 = Mo. \quad PbMoO_4 \times 0.3923 = MoO_3.$$

$$Mo \times 3.8241 = PbMoO_4. \quad MoO_3 \times 2.5491 = PbMoO_4.$$

Determination of Molybdenum as the Oxide, MoO_3

Determination by Precipitating with Mercurous Nitrate

Especially applicable where fusion with an alkali carbonate has been required.

Decomposition of Ore. One gram of the ore is fused with 4 grams of fusion mixture, ($Na_2CO_3 + K_2CO_3 + KNO_3$), and the cooled melt extracted with hot water.

If *manganese is present*, indicated by a colored solution, it may be removed by reduction with alcohol, the manganese precipitate filtered off and washed with hot water, the solution evaporated to near dryness and taken up with water, upon addition of nitric acid as stated below.

The solution containing the alkaline molybdate is nearly neutralized by adding HNO_3, the amount necessary being determined by a blank, and to the cold, slightly alkaline solution, a barely acid solution of mercurous nitrate is

added until no further precipitation occurs. The precipitate consists of mercurous molybdate and carbonate (chromium, vanadium, tungsten, arsenic and phosphorus will also be precipitated if present). The solution containing the precipitate is boiled and allowed to stand ten to fifteen minutes to settle, the black precipitate is filtered off and washed with a dilute solution of mercurous nitrate. The precipitate is dried and transferred as completely as possible to a watch-glass, the residue on the filter dissolved with hot dilute nitric acid, and the solution received in a large weighed porcelain crucible. The solution is evaporated to dryness on the water bath and the main portion of the precipitate added to this residue, and the whole heated very carefully over a low flame [1] until the mercury has completely volatilized. The cooled residue is weighed as MoO_3.

$$MoO_3 \times 0.6667 = Mo.$$

NOTE. If Cr, V, W, As or P are present a separation must be effected. Molybdenum should be precipitated in an H_2SO_4 solution in a pressure flask as the sulphide by H_2S as given in the following method, and arsenic if present removed by magnesia mixture as indicated in the procedure for separation of arsenic from molybdenum. If these impurities are present the molybdenum oxide may be fused with a very little Na_2CO_3, and leached with hot water and the filtrate treated with H_2S as directed.

Precipitation of Molybdenum as the Sulphide by H_2S

A. **Precipitation from Acid Solution.** By this procedure molybdenum is precipitated along with members of the hydrogen sulphide group, if present, but free from elements of the following groups.

The cold molybdenum solution slightly acid with sulphuric acid (in presence of Ba, Sr or Ca an HCl solution is necessary) is placed in a small pressure flask and saturated with H_2S, the flask closed and heated on the water bath until the precipitate has settled. The solution is cooled and filtered through a weighed Gooch crucible.

B. **Precipitation from an Ammoniacal Solution.** By this procedure molybdenum is precipitated with antimony, arsenic, tin if present, but is free from mercury, lead, bismuth, copper and cadmium.

Hydrogen sulphide is passed into the cold ammoniacal solution of molybdenum until it assumes a bright red color, it is now acidified with dilute sulphuric acid, the precipitate allowed to settle and the solution filtered through a weighed Gooch crucible.

In either case A or B the precipitate is washed into the Gooch crucible with very dilute sulphuric acid followed by several washings with the acid and then with alcohol until free from acid. The Gooch is placed within a larger nickel crucible and covered with a porcelain lid. After drying at 100° C. it is placed over a small flame and carefully heated until the odor of SO_2 can no longer be detected. The cover is now removed and the open crucible heated to constant weight. The residue consists of MoO_3.

$$MoO_3 \times 0.6667 = Mo.$$

NOTE. Arsenic will contaminate the residue if present. The method for its removal has been given.

[1] The oxide, MoO_3, sublimes at bright red heat.

VOLUMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM OR MOLYBDIC ACID

The Iodometric Reduction Method [1]

Principle. When a mixture of molybdic acid and potassium iodide in presence of hydrochloric acid is boiled, the volume having defined limits, free iodine is liberated and expelled and the molybdic acid reduced to a definite lower oxide; by titrating with a standard oxidizing agent the molybdic acid is determined.

Reaction. $2MoO_3+4KI+4HCl=2MoO_2I+I_2+4KCl+2H_2O$.

Reagents. N/10 solutions of iodine, sodium arsenite, potassium permanganate, sodium thiosulphate.

Analytical Procedure.[2] **Reduction.** The soluble molybdate in amount not exceeding an equivalent of 0.5 gram MoO_3 is placed in a 150-cc. Erlenmeyer flask, 20 to 25 cc. of hydrochloric acid (sp.gr. 1.2) added together with 0.2 to 0.6 gram potassium iodide. A short stemmed-funnel is placed in the neck of the flask to prevent mechanical loss during the boiling. The volume of the solution should be about 60 cc. The solution is boiled until the volume is reduced to exactly 25 cc. as determined by a mark on the flask. The residue is diluted immediately to a volume of 125 cc. and cooled. Either process *A* or *B* may now be followed.

A. **Reoxidation by Standard Iodine.** A solution of tartaric acid, equivalent to 1 gram of the solid, is now added, and the free acid nearly neutralized with sodium hydroxide solution (litmus or methyl orange indicator) and finally neutralized with sodium acid carbonate, $NaHCO_3$, added in excess. A measured amount of N/10 iodine is now run in. The solution is set aside in a dark closet for two hours, in order to cause complete oxidation, as the reaction is slow. The excess iodine is now titrated with N/10 sodium arsenite.

One cc. N/10 iodine = .0144 gram MoO_3 = .0096 gram Mo.

On long standing a small amount of iodate is apt to form. This is determined by making acid with dilute HCl and titrating with N/10 sodium thiosulphate.

B. **Reoxidation of the Residue by Standard Permanganate.** To the reduced solution about 0.5 gram of manganese sulphate in solution is added, followed by a measured amount of N/10 permanganate solution, added from a burette until the characteristic pink color appears. A measured amount of standard N/10 sodium arsenite, equivalent to the permanganate is then run in and about 3 grams of tartaric acid added. The acid is neutralized by acid sodium or potassium carbonate, the stopper and the sides of the flask rinsed into the main solution. The residual arsenite is now titrated by N/10 iodine, using starch indicator.

NOTES. Tartaric acid prevents precipitation during the subsequent neutralization with $NaHCO_3$. *A* and *B*.

The addition of manganese salt in *B* is to prevent the liberation of free chlorine by the action of $KMnO_4$ on HCl.

In addition to the oxidation of the lower oxides to molybdic acid, potassium permanganate added in *B* liberates free iodine from HI, it produces iodic acid, and forms the higher oxides of manganese. The standard arsenite, on the other hand, converts free iodine and the iodate to HI and reduces the higher oxides of manganese.

[1] F. A. Gooch and Charlotte Fairbanks, Am. Jour. Sc. (4), **2**, 160.
[2] F. A. Gooch and O. S. Pulman, Jr. Am. Jour. Sc. (4), **12**, 449.

Estimation by Reduction with Jones Reductor and Oxidation by Standard Permanganate Solution

Principle. The procedure depends upon the reduction of molybdic acid to Mo_2O_3 by passing its solution through a column of amalgamated zinc into a solution of ferric alum, and subsequent oxidation to MoO_3 by standard potassium permanganate solution.

Reactions. $2MoO_3+3Zn=Mo_2O_3+3ZnO.$

$$5Mo_2O_3+6KMnO_4+9H_2SO_4=10MoO_3+3K_2SO_4+6MnSO_4+9H_2O.$$

Reagents. *Potassium permanganate* approximately N/10 standardized against a standard molybdic acid solution.

10% solution of *ferric alum.*

2.5% solution of *sulphuric acid.*

Apparatus. *Jones Reductor.*

R = reductor tube 50 cm. long, 2 cm. inside diameter. Smaller tube prolongation length 20 cm. inside diameter 0.5 cm.

Zn = column of zinc 40 cm. long. *Zn* shot 8 mesh to sq.cm.;

F = receiving flask;

P = pressure regulator with gauge, set to give pressure in receiving flask of less than 20 cm. water;

G = platinum cone or gauze with mat of fine glass wool 2 cm. thick;

The zinc in reductor should be protected from the air by covering with water, stop-cock *S* being closed when not in use.

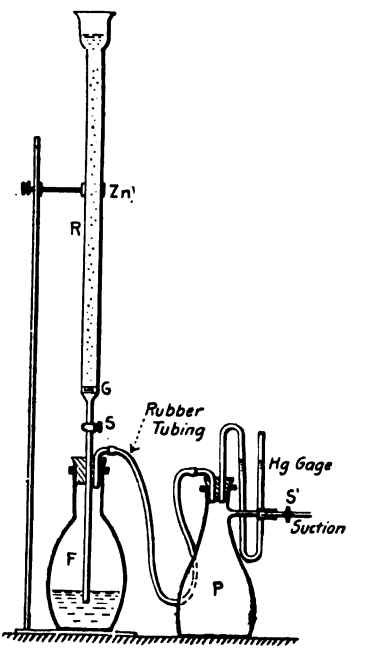


FIG. 49.—Jones Reductor.

Procedure. The receiving flask of the Jones reductor, Fig. 49, is charged with about 30 cc. of 10% ferric alum and 4 cc. of phosphoric acid.[2] Through the 40-cm. column of amalgamated zinc in the reductor are passed in succession 100 cc. of hot dilute sulphuric acid (2.5% sol.), the molybdic acid in the form of ammonium molybdate dissolved in 10 cc. of water and acidified with 100 cc. of hot dilute sulphuric acid followed by 200 cc. more of the hot dilute sulphuric acid and 100 cc. of hot water. The reduced green molybdic acid upon coming in contact with the ferric alum solution produces a bright red color.

The hot solution is titrated with N/10 $KMnO_4$ solution.

$$\text{One cc. of N/10 } KMnO_4=\frac{.0144}{3}\text{ gram } MoO_3=\frac{.0096}{3}\text{ gram molybdenum.}$$

[1] W. A. Noyes and Frohman, Jr. Am. Chem. Soc., **35**, 919.
See Method by C. R. Dudley, D. L. Randall, Am. Jr. Sc. (4), **24**, 313.

[2] C. Reinhardt, Chem. Ztg., **13**, 33.

Method for Determining Molybdenum and Vanadium in a Mixture of their Acids

Principle of the Method. The procedure depends upon the fact that vanadic acid alone is reduced by SO_2[1] in a sulphuric acid solution, whereas both vanadic and molybdic acids are reduced by amalgamated zinc, in each case the reducing agents forming definite lower oxides which are readily oxidized to definite higher oxides by $KMnO_4$.

Reactions.

SO_2 Reduction:

1. $V_2O_5+SO_2=V_2O_4+SO_3$. (No action on MoO_3.)

Zn Reduction:

2. $V_2O_5+3Zn=V_2O_2+3ZnO$.
3. $2MoO_3+3Zn=Mo_2O_3+3ZnO$.

$KMnO_4$ Oxidation:

4. $5V_2O_4+2KMnO_4+3H_2SO_4=5V_2O_5+K_2SO_4+MnSO_4+3H_2O$.
5. $5V_2O_2+6KMnO_4+9H_2SO_4=5V_2O_5+3K_2SO_4+6MnSO_4+9H_2O$.
6. $5Mo_2O_3+6KMnO_4+9H_2SO_4=10MoO_3+3K_2SO_4+6MnSO_4+9H_2O$.

From the reactions "4" and "5" it is seen that three times the amount of $KMnO_4$ is required to oxidize V_2O_2 to V_2O_5 as is required in the case of V_2O_4, hence—total cc. $KMnO_4$ required in oxidation of the zinc-reduced oxides minus three times the cc. $KMnO_4$ required in oxidizing the tetroxide of vanadium formed by the sulphur dioxide reduction = cc. $KMnO_4$ required to oxidize Mo_2O_3 to MoO_3. From these data molybdenum and vanadium may readily be calculated.

Method of Procedure. *A.* **Vanadic Acid.** The solution containing the vanadic and molybdic acids in a 250- to 300-cc. Erlenmeyer flask, is diluted to 75 cc. acidified with 2 to 3 cc. of strong sulphuric acid, heated to boiling and the vanadic acid reduced by a current of SO_2 passed into the solution until the clear blue color indicates the complete reduction of the vanadic acid to V_2O_4. The boiling is now continued and CO_2 passed into the flask to expel the last trace of SO_2.

Standard N/10 $KMnO_4$ is now run into the reduced solution to the characteristic faint pink. From reaction "4," vanadic acid may be calculated.

One cc. N/10 $KMnO_4$ = .0182 gram V_2O_5 = .0051 gram vanadium.

B. **Molybdic Acid.** The reduction by Jones' reductor, and titration of the combined acids reduced by amalgamated zinc with N/10 potassium permanganate solution, is carried out exactly as described in the determination of molybdic acid alone. In this case 50 cc. of 10% ferric alum and 8 cc. of the phosphoric acid is placed in the receiving flask.

Calculation. Total permanganate titration in *B* minus three times the titration in *A* gives the permanganate required to oxidize Mo_2O_3 to MoO_3. From equation 6 the molybdic acid may now be calculated.

$$\text{One cc. N/10 } KMnO_4 = \frac{.0144}{3} \text{ gram } MoO_3 = \frac{.0096}{3} \text{ gram molybdenum.}$$

[1] Reduction of vanadium by SO_2 in presence of molybdenum, Graham Edgar, Am. Jour. Sc., (4) **25**, 332. No reduction of MoO_3 when 0.4 gram is present with 5 cc. H_2SO_4 in 25 cc. volume.

For theoretical considerations and data on accuracy of method see "Methods in Chemical Analysis," F. A. Gooch.

NICKEL

W. L. Savell

Ni, *at.wt.* 58.68; *sp.gr.* 8.6–8.9; *m.p.* 1452° C; *b.p.*; *oxides*, NiO, Ni_2O_3, Ni_3O_4.

DETECTION

After bringing the sample into solution by one of the methods described under Preparation and Solution of the Sample, silica is removed, if present, in the usual manner, by evaporating the solution to dryness in the presence of an excess of hydrochloric acid, dissolving the residue and boiling with hydrochloric acid and filtering off the silica.

Hydrogen sulphide is then passed through the solution to remove the elements precipitated by this reagent. The filtrate from this precipitation is then boiled to expel the excess of hydrogen sulphide and a little nitric acid added to oxidize any ferrous iron to the ferric state. (See page 285, Separations.) Ammonium hydroxide is then added to precipitate iron, aluminum and chromium. Cobalt, nickel, manganese and zinc are precipitated from the filtrate by adding a solution of colorless ammonium sulphide or by passing hydrogen sulphide through the ammoniacal solution. Manganese and zinc are separated from the precipitate by washing with cold hydrochloric acid of about 1.035 sp.gr. A small quantity of the precipitate is fused with borax in the loop of a clean platinum wire. A green color in the cool bead indicates nickel. Fairly small quantities of cobalt interfere with this test, so if the bead is colored blue it will be necessary to make further tests for nickel.

Dimethylglyoxime will precipitate nickel as oxime from an acetic acid solution containing sodium acetate and in this manner separate it from cobalt, manganese and zinc. After precipitating iron, aluminum and chromium and filtering them off, the solution is slightly acidified with hydrochloric acid, then is neutralized with sodium hydroxide, and acidified with acetic acid. A solution of dimethylglyoxime is added, when nickel, if present, will be precipitated as a flocculent red precipitate.

Nickel may be detected in the presence of cobalt by adding a solution of sodium hydroxide to the solution of cobalt and nickel until a slight precipitate is formed, then somewhat more potassium cyanide than is necessary to redissolve the precipitate and finally two volumes of bromine water. Warm gently and allow to stand for some time. If a precipitate of nickel hydroxides separates, filter, wash and test with the borax bead.

Nickel may also be detected in the presence of cobalt by precipitating the cobalt as nitrite, as described in the chapter on cobalt, and then precipitating the nickel as hydroxide with sodium hydroxide and bromine water and testing the precipitate with the borax bead.

Alpha benzildioxime added to an ammoniacal solution of nickel precipitates an intensely red salt having the composition $C_{28}H_{22}N_4O_4Ni$. This precipitate is very voluminous. Silver, magnesium, chromium, manganese and zinc do not interfere with this reaction.

ESTIMATION

The determination of nickel is required, principally, in the analysis of ores, metallic nickel and its alloys, but is also required in the analysis of metallic cobalt and cobalt products as well as in a host of miscellaneous materials.

In the majority of cases the results of a nickel determination are calculated in terms of metallic nickel. Even in the determination of nickel in nickel-plating solution the results are calculated in terms of metallic nickel since this is the factor by which the solutions are controlled.

Preparation and Solution of the Sample

The materials in which nickel occurs ordinarily, may, in general, be brought into solution by treatment with acids, but in the case of some refractory ores and alloys, a fusion is required first to make the acid treatment effective. When treating ores containing sulphides or arsenides a strong oxidizing treatment is necessary to break up these compounds. Metallic nickel may be dissolved easily in nitric acid, more slowly in hydrochloric acid and still more slowly by sulphuric. Nickel alloys may be dissolved in a mixture of hydrochloric acid and nitric acid.

General Procedure for Ores. One gram of the finely powdered ore is weighed into a porcelain dish and mixed intimately with 3 grams of powdered potassium chlorate. The dish is covered with a watch-glass and 40 cc. concentrated nitric acid added slowly. The dish is allowed to stand in a cool place for a few minutes, then placed on a water bath and digested until the sample is completely decomposed, stirring the mixture frequently with a glass stirring rod, and adding a little potassium chlorate from time to time until the decomposition is complete. The watch-glass is then removed and any particles that may have spattered on it are washed back into the dish and the evaporation continued to dryness. This evaporation to dryness is repeated with the addition of 10 cc. of concentrated hydrochloric acid, and the silica dehydrated by heating for an hour or more in an air oven at 110° C. The dry residue is moistened with concentrated hydrochloric acid and the sides of the dish washed down with hot water, the mixture heated to boiling and allowed to boil for a few minutes, then withdrawn from the heat and filtered, hot, after the insoluble matter has settled.

Treat the filtrate for the removal of interfering elements as directed under Separations.

Fusion Method. The above method is used where it is desired to determine insoluble matter or " gangue." As a method of bringing the nickel in the sample into solution it is quite satisfactory and when the insoluble matter burns to a pure white ash the ignited residue may be weighed as silica, but in some cases this method does not give sufficient information regarding the composition of the gangue.

If it is necessary to make a complete analysis it is usually better to fuse the sample with the sodium and potassium carbonate mixture containing a little potassium nitrate and then treat in the usual manner to determine silica.

Potassium Bisulphate Fusion. In the treatment of nickel and cobalt oxides these are ground to a fine powder and a representative sample of 1 gram is fused with 10 grams of potassium bisulphate. This may be done in a porcelain or silica crucible or dish. The melt is extracted with water and the silica filtered off.

A small casserole has been found to be very useful for this fusion.

Solution of Metallic Nickel and Its Alloys. From 1 to 5 grams of the well-mixed drillings are treated with a minimum quantity of nitric acid and 20 cc. 1 : 1 sulphuric acid added and the solution evaporated to fumes of sulphur trioxide. Allow the fuming to continue for ten minutes. Dilute carefully with a little water and filter off the insoluble. Continue as directed in the following detailed analyses.

It may be necessary to use a mixture of nitric and hydrochloric acids to bring certain alloys into solution, after which the procedure is the same as above.

SEPARATIONS

Separation of the Ammonium Sulphide Group, Containing Nickel from the Hydrogen Sulphide Group. Mercury, Lead, Bismuth, Copper, Cadmium, Arsenic, Antimony, Tin, Gold, Molybdenum, etc.

The hydrogen sulphide group elements are precipitated from an acid solution (HCl) by H_2S, and removed by filtration, nickel, etc., passing into the filtrate.

Separation of the Ammonium Sulphide Group from the Alkaline Earths and Alkalies. Nickel is precipitated with other members of the group by passing H_2S into its ammoniacal solution, or by adding $(NH_4)_2S$ solution. The alkaline earths and alkalies are not precipitated.

Separation of Nickel from Cobalt. This procedure can be carried out in exactly the same manner as the method given for the determination of nickel by precipitation of nickel with dimethylglyoxime, since cobalt is soluble as oxime. In case more cobalt is present than nickel a larger excess of the reagent must be used. The excess of acid is best neutralized with ammonium hydroxide. If both metals are to be determined, cobalt may be determined electrolytically in the filtrate.

An alternate method is to determine the cobalt and nickel as oxides, or metal by electrolysis, together. The oxides, or plate, are dissolved in nitric acid and the nickel determined in the solution, cobalt being found by difference.

For other methods see Separation of Cobalt from Nickel, under Cobalt, page 142.

Separation of Nickel from Manganese. Nickel is precipitated by dimethylglyoxime from an acetic acid solution containing sodium acetate, manganese being determined in the filtrate.

Separation of Nickel from Zinc. Zinc does not interfere in the dimethylglyoxime precipitation of nickel when ammonium salts are present. It is advisable to precipitate the nickel in a dilute acetic acid solution, thus avoiding the addition of a large amount of ammonium salts as would be necessary if the precipitation took place in an ammoniacal solution. Zinc readily remains in solution, and may be determined in the filtrate from the nickel oxime precipitate. The following procedure is recommended:

The solution containing the two metals is neutralized with ammonium hydroxide and then made just slightly acid with acetic acid and sodium acetate added. Dimethylglyoxime solution is now added to the solution, which is nearly boiling, and the procedure given for the determination of nickel by this reagent is followed.

Separation of Nickel from Iron. Nickel cannot be separated satisfactorily from iron by precipitating the latter with ammonium hydroxide, as some of the nickel is invariably occluded by the ferric hydroxide precipitate. Two modifications of the oxime method may be used.

(1) The iron, if present as a ferric salt, is converted into a complex salt by

adding from 1 to 2 grams of tartaric acid, and the solution diluted to 200 or 300 cc., boiled and the nickel precipitated as the oxime in an ammoniacal solution by the prescribed method. Iron forms no oxime under these conditions.

The iron may be precipitated from this filtrate by colorless ammonium sulphide and the sulphide converted to ferric oxide (Fe_2O_3) by ignition.

(2) Ferric iron is reduced to the ferrous condition by warming with sulphurous acid, in a nearly neutral solution. If the original solution has an excess of acid, it is treated with a solution of sodium hydroxide until a permanent precipitate is formed. This is dissolved with a few drops of hydrochloric acid and the iron reduced by adding from 5 to 10 cc. of a saturated solution of sulphur dioxide or by passing dioxide through the solution. The solution is diluted to 200 or 300 cc. and the solution of dimethylglyoxime added in slight excess, followed by sodium acetate until a permanent precipitate of nickel oxime is formed. After adding 2 grams more of sodium acetate the solution is filtered immediately. The iron is precipitated from the filtrate by oxidizing with bromine water and adding ammonium hydroxide to precipitate the basic acetate of iron.

Procedure (1) is suitable for the determination of nickel in iron and steel.

Separation of Nickel from Aluminum. This method is the same as procedure (1) given above.

Separation of Nickel from Chromium. This separation cannot be carried out in an acetic acid solution. From 1 to 2 grams of tartaric acid are added and from 5 to 10 cc. of a 10% ammonium chloride solution, subsequently. The solution is made ammoniacal, but no precipitate should form. If the solution becomes cloudy, it is acidified with hydrochloric acid and additional ammonium chloride added and again made ammoniacal and the nickel precipitated as oxime according to directions given from this precipitation.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF NICKEL

Precipitation of Nickel by Alpha Benzildioxime

The alcoholic solution of alpha benzildioxime gives an intensely red precipitate of $C_{28}H_{22}N_4O_4Ni$, when added to ammoniacal solutions containing nickel. The reaction is more characteristic for nickel than is that with dimethylglyoxime and is more delicate. In a volume of 5 cc. (according to F. H. Atack), 1 part of nickel in 2,000,000 parts of water may be detected. In the presence of 100 times as much as cobalt only a faint yellow color is produced by the cobalt. One part of nickel per million of water will cause precipitation with the compound, whereas no precipitate is formed with dimethylglyoxime under the same conditions. With glyoxime iron produces a pink color, with alpha benzildioxime ferrous salts give a faint violet color, hence do not interfere in the detection of nickel. Silver, magnesium, chromium, manganese, and zinc do not interfere. Since the nickel precipitate with this reagent is exceedingly voluminous it is advisable to have not more than 0.025 gram of nickel in the solution in which the nickel is being determined. The method is adapted to the detection and determination of minute traces of the element up to small amounts of less than 10% nickel.

Reagent, Alpha Benzildioxime. This may be prepared by boiling 10 grams of benzil (not necessarily pure) with 8 to 10 grams of hydroxylamine hydrochloride in methyl alcohol solution. After boiling for three hours the precipitate is filtered off and dried, washed with hot water and then with a small amount of 50% alcohol, and dried. This dried precipitate consists of pure benzildioxime (m.p. 237° C.). A further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride. The reagent is prepared by dissolving 0.2 gram of the salt per liter of alcohol to which is added ammonium hydroxide to make 5% solution, sp.gr. 0.96 (50 cc. per liter).

Procedure. A slight excess of the warmed solution of the above reagent is stirred into the ammoniacal solution containing nickel and the whole heated on the water bath for a few moments to coagulate the precipitate. Quantitative precipitation is complete after one minute. The liquid is filtered through a Gooch crucible, with suction, or onto a filter paper, for which a counterpoise has been selected. The counterpoise paper is treated in exactly the same manner as the one containing the precipitate. The precipitate is washed with 50% alcohol, followed by hot water, and is then dried at 110° C. In weighing the precipitate the counterpoise filter is placed in the weight pan of the balance. The precipitate contains 10.93% nickel. Weight of $C_{28}H_{22}N_4O_4Ni \times 0.01093 = Ni$.

NOTES. Acetone may be used instead of alcohol as a solvent of the reagent. The compound is more soluble in acetone than in alcohol.

The precipitate does not pass through the filter as does the compound with dimethylglyoxime.

The method is affected by the presence of nitrates, hence these must be removed by evaporation of the solution with sulphuric acid to fumes, before the addition of the reagent to the nickel solution.

In the presence of cobalt an excess of the reagent must be used, as in the case of the dimethylglyoxime precipitation.

In the presence of iron and chromium Rochelle salt, sodium citrate or tartaric acid are added to prevent precipitation of the hydroxides of these metals upon making the solution alkaline.

In the presence of manganese a fairly large excess of the reagent is required, the solution being slightly acid with acetic acid.

Zinc and magnesium are kept in solution by addition of ammonium chloride.

Large amounts of copper must be removed by precipitating with hydrogen sulphide before addition of the reagent.

The nickel salt with the reagent forms an extremely voluminous precipitate so that a concentration of 0.09 gram of nickel per 250 cc. is as high as is desirable. The process is applicable to the determination of nickel in the filtrate obtained in the separation of zinc after the removal of the hydrogen sulphide, formic acid, etc.

Method by F. W. Atack, The Analyst, **38**, 448, 318. Cockburn, Gardiner and Black, Analyst, **38**, 439, 443.

Precipitation of Nickel by Dimethylglyoxime

Preliminary Considerations. This method has been demonstrated by O. Brunck to be the most accurate and expeditious procedure known for nickel.[1] By this method 1 part of nickel may be detected when mixed with 5000 parts of cobalt or 1 part of nickel may be detected in 400,000 parts of water. The nickel precipitate with this reagent is almost completely insoluble in water and is only very slightly soluble in acetic acid, but is easily decomposed by strongly dissociated acids, so that the precipitation is incomplete in neutral solutions of nickel chloride, sulphate or nitrate. If, however, the free acid formed is neutral-

[1] Zeit. f. ang. Chem., **20**, 1844.

ized with sodium, potassium or ammonium hydroxides or by addition of the acetate salts of these bases, nickel will be completely precipitated, not even a trace being found in the filtrate.

"The quantitative determination of nickel in the presence of other metals is a simple operation. The nickel should be in the form of a convenient salt.

"The concentration of the solution does not matter; the precipitation can take place either in a solution of the greatest concentration, or in a very dilute solution. The reaction is not hindered by the presence of ammonium salts."

Iron, aluminum, chromium, cobalt, manganese and zinc do not interfere. Theoretically 4 parts of dimethylglyoxime, added as a 1% alcoholic solution, are necessary; a certain excess does no harm provided the alcohol volume does not exceed more than half that of the water solution containing the nickel salt, as alcohol has a solvent action on the oxime. The compound is very stable and volatilizes undecomposed at 250° C.

An excess of ammonium hydroxide is also to be avoided in the solution in which the precipitation takes place.

It has been observed that the precipitate of nickel with dimethylglyoxime may be safely ignited to the oxide NiO without loss, if the filter is first carefully charred without allowing it to take fire, then gradually heated to redness.

Procedure. Such an amount of the sample should be taken that the nickel be not over 0.1 gram, as glyoxime of nickel is very voluminous and a larger amount would be difficult to filter. If cobalt is present it should not exceed 0.1 gram in the sample taken.[1]

If hydrogen sulphide has been used to precipitate members of the second group, it is expelled by boiling the acid solution and the volume brought to 250 cc.

One or 2 grams of tartaric acid are added to prevent the precipitation of the hydroxides of iron, aluminum and chromium by ammonium hydroxide (this treatment is omitted if these are absent), and 5 to 10 cc. of a 10% solution of ammonium chloride added to keep zinc and manganese in solution, should they be present. Ammonium hydroxide is now added until the solution is slightly alkaline. If a precipitate forms, ammonium chloride is added to clear the solution, followed by ammonium hydroxide to neutralize the acid. The solution should remain clear after this treatment, otherwise the ammonium chloride is added in solution or as salt until the solution of the sample will remain clear. It is then heated to nearly boiling and the alcoholic solution of dimethylglyoxime added until the reagent is approximately seven times, by weight, the weight of nickel present. Ammonium hydroxide is now added until the solution has a distinct odor of this reagent. The precipitation of the scarlet red nickel salt is hastened by stirring. It is advisable to place the mixture on the steam bath for fifteen to twenty minutes to allow the reaction to go to completion before filtering. The precipitate is filtered off, into a platinum sponge Gooch crucible, sometimes known as a Neubauer Gooch crucible. (Other forms of Gooch crucible are used for this purpose, but the Neubauer crucible has been found to be most satisfactory.) The precipitate is dried for about two hours at 110 to 120° C. and weighed as $C_8H_{14}N_4O_4Ni$, which contains 20.32% Ni.

Weight of precipitate multiplied by 0.2032 = weight of nickel.

[1] If the sample contains more than 0.1 gram of cobalt, a large excess of ammonium hydroxide and dimethylglyoxime is necessary to prevent its precipitation, hence it is advisable to take such weights of samples that the cobalt content will be less than this weight.

In place of a Gooch crucible a tared filter paper may be used. It must be remembered, however, that a blank filter paper of the same kind as used for the precipitate must be used as a counterbalance, after treating in exactly the same manner as the one containing the precipitate. This is necessary because it has been found that filter paper loses weight during washing and drying.

Precipitation of Nickel by Electrolysis [1]

This precipitation is conducted in exactly the same manner as the one described under Cobalt for the Precipitation of Cobalt by Electrolysis, and requires that the same precautions be exercised in the practice of the method.

In the presence of cobalt the two elements may be determined together by electrolysis as described below and the deposited metal redissolved and the two elements separated by one of the methods given under Cobalt or Nickel.

Procedure. After the sample has been brought into solution by one of the methods outlined under Preparation and Solution of the Sample, the solution is evaporated with 20 cc. of 1 : 1 sulphuric acid for every gram of metal in the sample. The evaporation is continued until the solution has fumed strongly for ten minutes. Cool carefully and dilute with 20 cc. of water. Heat the solution to nearly boiling and pass hydrogen sulphide for one hour to precipitate members of the second group. This long treatment is necessary to insure complete precipitation of arsenic. Filter and boil to expel hydrogen sulphide. Add 5 cc. nitric acid to insure oxidation of iron compounds to the ferric state and add ammonium hydroxide until just slightly alkaline. Filter off the ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. To recover occluded nickel dissolve the precipitate in hydrochloric acid and reprecipitate the iron with addition of a little hydrogen peroxide. Combine the filtrates. Evaporate to about 250 cc. and add 50 cc. of strong ammonium hydroxide and electrolyze as described under Cobalt, page 144.

The increase in weight of the electrode is the weight of cobalt and nickel in the sample. The percentage of cobalt and nickel in the sample is found by multiplying the increase in weight of the electrode by 100 and dividing by the weight of the sample.

NOTE. The deposition of cobalt and nickel by the above method has been found to be the most accurate of the electrolytic methods. In the solutions containing the organic acids there is always more or less carbide deposited on the cathode with the metal. This causes high results.

Nickel in Metallic Nickel

This determination may be made in the manner described under Precipitation of Nickel by Electrolysis, separating cobalt before or after the electrolysis or by the method described under Precipitation of Nickel by Dimethylglyoxime. The latter method is recommended.

Nickel in Cobalt and Cobalt Oxide

The dimethylglyoxime precipitation is used in combination with the electrolytic precipitation. See chapter on Cobalt.

[1] W. J. Marsh, J. Phys. Chem., 18, 705–16, 1914.

VOLUMETRIC DETERMINATION OF NICKEL

Determination of Nickel in Alloys

This method, as described by S. W. Parr and J. M. Lindgren,[1] consists of a modification of the dimethylgloxime method. The precipitation takes place in the usual manner and the precipitate is dissolved in sulphuric acid and the excess titrated with a standard solution of potassium hydroxide.

Procedure. The alloy is dissolved in nitric or hydrochloric acids and if iron, aluminum or chromium are present twice their weight of tartaric acid is added to prevent their precipitation. If chromium is present ammonium chloride is also added. If manganese or zinc is present hydrochloric acid should be used and most of the free acid evaporated. Add a few cc. of hydrogen peroxide to oxidize any ferrous iron to the ferric state. Dilute to 300 or 400 cc. and neutralize the free acid by sodium acetate. Heat the solution to nearly boiling and add five times as much dimethylglyoxime, in 1% alcoholic solution, as the nickel present. Then completely neutralize with ammonium hydroxide, using a very slight excess (or the solution may be neutralized with sodium acetate). Heat until all the nickel is precipitated. Filter and wash. Place the precipitate and filter in a beaker, add an excess of 0.05N sulphuric acid, dilute to 200 cc., heat until solution is complete and titrate back with 0.1N potassium hydroxide solution, taking the first faint yellowish tinge as the end-point. The solutions are standardized against pure nickel.

NOTE. Cobalt should not exceed 0.1 gram per 100 cc. and an excess should be used of the dimethylglyoxime.

Nickel in Nickel-plating Solutions

In most cases it is quite unnecessary to separate the cobalt from the nickel in making this determination and, as the principal impurity is usually iron, the best practice is to follow the method given under Precipitation of Cobalt by Electrolysis, page 144.

If chlorides or organic matter are present in the solution the preparation of the solution for electrolysis is accomplished in the following manner:

From the well-stirred solution in the plating tank, withdraw about 200 cc. and place in a small beaker. Prepare a 100-cc. burette by thoroughly cleaning it with the sulphuric acid and potassium bichromate mixture and distilled water. Wash finally with a few cc. of the nickel solution and fill the burette with the solution from the plating tank.

Run 66.7 cc. into an evaporating dish and add 2 cc. 1 : 1 sulphuric acid. Evaporate to fumes of sulphur trioxide and allow to fume strongly for ten minutes. Dissolve in a little water. Dilute to 200 cc. carefully, neutralize with a solution of ammonium hydroxide and add 50 cc. of strong ammonium hydroxide and electrolyze. (See Precipitation of Cobalt by Electrolysis.)

The increase in weight of the cathode in grams multiplied by 2 gives the weight in ounces of nickel in one United States gallon of the plating solution.

[1] S. W. Parr and J. M. Lindgren, Trans. Am. Brass Founders' Assoc., 5, 120–9.

NITROGEN

WILFRED W. SCOTT

Element. **N_2,** ***at.wt.*** **14.01; D. (*air*) 0.9674;** ***m.p.*** **$-210°$;** ***b.p.*** **$-195.5°$ C.;** ***oxides,*** **N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5.**

Ammonia. **NH_3,** ***m.w.*** **17.03; D. (*air*) 0.5971;** ***sp.gr. liquid*** **0.6234;** ***m.p.*** **$-77.3°$;** ***b.p.*** **$-38.5°$ C.** ***Crit. temp.*** **130°;** ***liquid at*** **0°** ***with*** **4.2** ***atmospheres pressure.*** ***Commercial*** **28% NH_3,** ***sp.gr.*** **0.90.**

Nitric Acid. **HNO_3,** ***m.w.,*** **63.02;** ***sp.gr.*** **1.53;** ***m.p.*** **-41.3;** ***b.p.*** **86° C.** ***Boiling-point of commercial*** **95%** ***acid is a little above*** **86°,** ***but gradually rises to*** **126°** ***and the strength of acid falls to*** **68.9%,** ***sp.gr. is then*** **1.42.** ***The acid now remains constant, the distillate being of the same strength.***

DETECTION

Element. Organic Nitrogen. Organic matter is decomposed by heating in a Kjeldahl flask with concentrated sulphuric acid as described under preparation and solution of the sample. Ammonia may now be liberated from the sulphate and so detected.

Nitrogen in Gas. Recognized by its inertness towards the reagents used in gas analysis. The element may be recognized by means of the spectroscope.

Ammonia. Free ammonia is readily recognized by its characteristic odor. A glass rod dipped in *hydrochloric acid* and held in fumes of ammonia produces a white cloud of ammonium chloride, NH_4Cl.

Moist red litmus paper is turned blue by ammonia. Upon heating the paper the red color is restored, upon volatilization of ammonia (distinction from fixed alkalies).

Nessler's Test.[1] Nessler's reagent added to a solution containing ammonia, combined or free, produces a brown precipitate, $NHg_2I \cdot H_2O$. If the ammoniacal solution is sufficiently dilute a yellow or reddish-brown color is produced, according to the amount of ammonia present. The reaction is used in determining ammonia in water.

Salts of ammonia are decomposed by heating their solutions with a strong base such as the hydroxides of the fixed alkalies or the alkaline earths. The odor of ammonia may now be detected.

Nitric Acid. ***Ferrous Sulphate Test.*** About 1 to 2 cc. of the concentrated solution of the substance is added to 15 to 20 cc. of strong sulphuric acid in a test-tube. After cooling the mixture, the test-tube is inclined and an equal volume of a saturated solution of ferrous sulphate is allowed to flow slowly down over the surface of the acid. The tube is now held upright and gently tapped. In the presence of nitric acid a brown ring forms at the junction of the two solutions.

[1] The reagent is made by dissolving 20 grams of potassium iodide in 50 cc. of water, adding 32 grams of mercuric iodide and diluting to 200 cc. To this is added a solution of potassium hydroxide—134 grams KOH per 260 cc. H_2O.

The test for nitrate may be made according to the quantitative procedure given for determining of nitric acid (see later). It should be remembered that ferrous sulphate should be present in excess, otherwise the brown color is destroyed by the free nitric acid. Traces of nitric acid in sulphuric produce a pink color with the sulphuric acid solution of ferrous sulphate. (See Determination of Nitric Acid—Ferrous Sulphate Method.)

Ferro- and ferricyanides, chlorates, bromides and bromates, iodides and iodates, chromates and permanganates interfere.

Diphenylamine Tests for Nitrates. $(C_6H_5)_2NH$ dissolved in sulphuric acid is added to 2 or 3 cc. of the substance in solution on a watch-glass. Upon gently warming a blue color is produced in presence of nitrates. Nitric acid in sulphuric acid is detected by placing a crystal of diphenylamine in 3 or 4 cc. of the acid and gently warming. Cl', Cl^{V}, Br^{V}, I^{V}, Mn^{VII}, Cr^{VI}, Se^{IV}, Fe''' interfere.

Copper placed in a solution containing nitric acid liberates brown fumes.

Phenolsulphonic Acid Test. See chapter on Water Analysis.

Detection of Nitrous Acid. ***Acetic Acid Test.*** Acetic acid added to a nitrite in a test-tube (inclined as directed in the nitric acid test with ferrous sulphate), produces a brown ring. Nitrates do not give this. If potassium iodide is present in the solution, free iodine is liberated. The free iodine is absorbed by chloroform, carbon tetrachloride or disulphide, these reagents being colored pink. Starch solution is colored blue.

Nitrous acid reduces iodic acid to iodine. The iodine is then detected with starch, or by carbon disulphide, or carbon tetrachloride.

Potassium Permanganate Test. A solution of the reagent acidified with sulphuric acid is decolorized by nitrous acid or nitrite. The test serves to detect nitrous acid in nitric acid. Other reducing substances must be absent.

ESTIMATION

Occurrence. Element. Free in air to extent of 78%+ by volume and 76%− by weight.

Air weight of 1 liter = 1.293 grams. With oxygen as 32, air = 28.95.

COMPOSITION OF AIR. ON THE BASIS OF 1000 LITERS OF ATMOSPHERE

Element.	Liters per 1000 l.	Weight per 1000 l. grams	Per cent by Vol.	Per cent by Wt.
Nitrogen	780.3	975.80	78 1	75.47−
Oxygen	209.9	299.84	21.0	23.19−
Argon	9.4	16.76	0.9	1.296+
Carbon dioxide	0.3	0.59	0.04	0.045
Hydrogen	0.1	0.01		
Neon	0.015	0 01339		
Helium	0.0015	0.00027		
Krypton	0.00005	0.00018		
Xenon	0.000006	0.00003		

Water-saturated air contains 2.4 grams H_2O at −10°; 4.9 grams at 0°; 17.2 grams at 20° and 55 grams H_2O at 40° C. Ordinarily 50 to 70% of this is present.

Nitrogen is found combined in nature as potassium nitrate (saltpeter), KNO_3; sodium nitrate (Chili saltpeter), $NaNO_3$, and to a less extent as calcium nitrate,

$Ca(NO_3)_2$. It occurs in plants and in animals, in the substances proteids, blood, muscle, nerve substance, in fossil plants (coal), in guano, ammonia and ammonium salts.

Free nitrogen is estimated in the complete analysis of gas mixtures. In illuminating gas the other constituents are removed by combustion and absorption and the residual gas measured as nitrogen.

Total nitrogen in organic substances is best determined by decomposition of the materials with sulphuric acid as described later, and estimating the nitrogen from the ammonia formed.

Combined nitrogen in the form of ammonia and nitric acid specially concerns the analyst. In the evaluation of fertilizers, feedstuffs, hay, fodders, grain, etc., the nitrogen is estimated after conversion to ammonia. Ammonia, nitrates and nitrites may be required in an analysis of sewages, water, and soils. Nitric acid is determined in Chili saltpeter, in the evaluation of this material for the manufacture of nitric acid or a fertilizer, the nitrate being reduced to ammonia and thus estimated.

We will take up a few of the characteristic substances in which nitrogen estimations are required, e.g., in organic substances as proteids, in soils and fertilizers; in ammonium salts, nitrates, and nitrites, free ammonia in ammoniacal liquors, nitric acid in the evaluation of the commercial acid and in mixed acids.

In general nitrogen is more accurately and easily measured as ammonia, to which form it is converted by reduction methods. Large amounts are determined by titration, whereas small amounts are estimated colorimetrically. Nitric acid and nitrates may be determined by direct titration by the Ferrous Sulphate Method outlined later. The procedure is of value in estimation of nitrates in mixed acids. The nitrometer method for determining nitrates (including nitrites), and the free acid in mixed acids, is generally used by manufacturers of explosives.

Preparation of the Sample

It will be recalled that compounds of ammonia and of nitric acid are generally soluble in water. All nitrogen compounds, however, are not included. Among those which are not readily soluble the following deserve mention: compounds of nitrogen in many organic substances; nitrogen bromophosphide, $NPBr_2$; nitrogen selenide, NSe; nitrogen sulphide, N_4S_4; nitrogen pentasulphide, N_2S_5; ammonium antimonate, $NH_4SbO_3 \cdot 2H_2O$; ammonium iodate, HN_4IO_3 (2.6 grams per 100 cc. H_2O); ammonium chlorplatinate, $(NH_4)_2PtCl_6$ (0.67 gram); ammonium chloriridate, $(NH_4)_2IrCl_6$ (0.7 gram); ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$ (4.2 grams); ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$ (0.03 gram); nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$.

Organic Substances

By oxidation of nitrogenous organic substances with concentrated sulphuric acid, containing mercuric oxide, or potassium permanganate, the organic matter is destroyed and the nitrogen is changed to ammonia, which is held by the sulphuric acid as sulphate. Nitrates are reduced by addition of salicylic acid, zinc dust, etc., previous to the oxidation process. Practically all the procedures are based on the Kjeldahl method of acid digestion. The modification, commonly known as the Kjeldahl-Gunning-Arnold Method, is as follows:

Method in Absence of Nitrates. ***Weight of Sample.*** ***Fertilizers*** 0.7 to 3.5 grams. *Soils* 7 to 14 grams. *Meat* and *meat products* 2 grams. *Milk* 5 grams. The amount of the substance to be taken should be governed by its nitrogen content.[1]

Acid Digestion.[2] The material is placed in a Kjeldahl flask of about 550 cc. capacity. Approximately 0.7 gram of mercuric oxide or an equivalent amount of metallic mercury together with 10 grams of powdered potassium sulphate followed by 20 to 30 cc. of concentrated sulphuric acid (sp.gr. 1.84) are added. The flask is placed in an inclined position, resting in a large circular opening of an asbestos board. The flask is heated with a small flame until the frothing has ceased. (A piece of paraffin may be added to prevent extreme frothing.) The heat is then raised and the acid brought to brisk boiling, the heating being continued until the solution becomes a pale straw color, or practically water white. (In case of leather, scrap, cheese, milk products, etc., a more prolonged digestion may be required. With a good flame from one-half to one hour of acid digestion is generally sufficient to completely decompose the material.) The flask is now removed from the flame and after cooling the solution is diluted with about 200 cc. of water and a few pieces of granulated zinc added to prevent "bumping" (50 mg. or so of No. 80 granulated zinc). The solution is now alkalized strongly by addition of a mixture of sodium hydroxide and sodium sulphide solution (about 75 cc. of a mixture containing 25 grams of NaOH and 1 gram Na_2S). Phenolphthalein indicator added to the solution will show when the acid is neutralized. The flask is connected by means of a Hopkins distillation tube (Fig. 53) to a condenser and about 150 cc. of the solution distilled into an excess of standard sulphuric acid and the excess of the acid determined by titration with standard sodium hydroxide. (Methyl red indicator.)

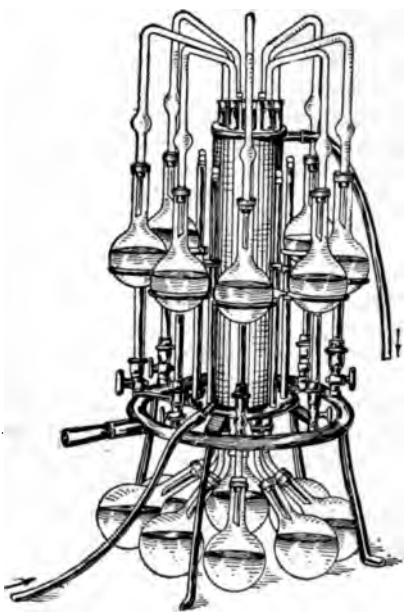


FIG. 50.
Apparatus for Determining Nitrogen.

The ammonia may be absorbed in a saturated solution of boric acid and titrated directly with standard acid. (Methyl orange indicator.)[3]

One cc. N/10 H_2SO_4 = 0.001704 gram NH_3.

[1] See data of approximate nitrogen content in certain nitrogenous substances, Jour. Ind. Eng. Chem., 7, 357, 1915.

[2] Fig. 50 shows a compact apparatus with several sets of flasks and condensers, which enable half a dozen or more determinations to be made at one time.

[3] L. W. Winkler, Z. angew. Chem., 27, 1, 630–2, 1914. E. Bernard, ibid., 27, 1, 664, 1914.

In Presence of Nitrates. The procedure differs from the former in the preliminary treatment to reduce the nitrates. The material in the flask is treated with a mixture of 30 to 35 cc. of strong sulphuric acid containing 1 gram of salicylic acid and the mixture shaken and allowed to stand for five to ten minutes with frequent agitation. About 5 grams of sodium thiosulphate are now added and the solution heated for five minutes. After cooling, mercuric oxide or metallic mercury and potassium sulphate are added, and the solution treated as directed above.

NOTES. Mercuric oxide or metallic mercury are added as a catalyzer to assist the oxidation of the organic matter. The digestion process is shortened considerably by its use. In place of mercuric oxide or the metal, copper sulphate may be used. In this case the addition of sodium sulphide is omitted. Copper sulphate acts as an indicator in the neutralization of the sample with caustic.

Potassium sulphide is added to remove the mercury from the solution and prevent the formation of mercur-ammonium compounds, which are not completely decomposed by sodium hydroxide.

A blank determination should be made on the reagents used with sugar as the organic substance.

Soils. Available Nitrates. Five hundred to 1000 grams of the air-dried soil is extracted with 1 to 2 liters of water containing 10 to 20 grams of dextrose. Fifteen to twenty hours of leaching is sufficient. An aliquot portion is taken for analysis.

Ammonium Salts. The sample is placed in the distillation flask with splash bulb as described in the modified Kjeldahl procedure for organic substances, and the material decomposed with ammonia-free caustic solution. The ammonia is distilled into an excess of standard acid or a saturated solution of boric acid (neutral to methyl orange), and the ammonia determined as usual, either by titration of the excess of acid, or by direct titration with acid, according to the absorbent used.

Nitrates. The sample, broken down as fine as possible, is dissolved in water, decomposed with Devarda alloy and distilled as described by the modified Devarda methods given later.

Nitrites. The material, dissolved in water, is titrated with standard permanganate solution according to the procedure described later.

Mixtures of Ammonium Salts, Nitrates, and Nitrites. Ammonia is determined by distillation with caustic as usual. The nitrite is titrated with permanganate. Total nitrogen is determined by the modified Devarda methods. Nitric acid is now estimated by difference, e.g., from the total nitrogen is deducted the nitrogen due to ammonia together with the nitrogen of the nitrite and the difference calculated to the nitrate desired. The nitrate may be determined in presence of nitrite and ammonia by direct titration with ferrous sulphate. The detailed procedures may be found under the Volumetric Methods.

Nitric Acid in Mixed Acid. This is best determined by the ferrous sulphate method for nitric acid. The nitrometer method is also excellent.

SEPARATIONS

Ammonia. No special separation need be considered in the determination of ammonia. The general method has already been mentioned by which ammonia is liberated from its salts by a strong base and volatilized by heat. This effects a separation from practically all substances.

Nitric Acid. The compound may be isolated as the fairly insoluble, crystalline nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$ by the following procedure.

Such an amount of the substance is taken as will contain about 0.1 gram nitric acid, and dissolved in about 100 cc. of water with addition of 10 drops of dilute sulphuric acid. The solution is heated nearly to boiling and about 12 cc. of nitron acetate solution added (10 grams of nitron in 100 cc. of 5% acetic acid).[1] The solution is cooled and placed in an ice pack for about two hours, and the compound then transferred to a Gooch or Munroe crucible (weighed crucible if gravimetric method is to be followed), and after draining, it is washed with about 10 to 12 cc. of ice-water added in small portions. The nitrate may now be determined gravimetrically by drying the precipitate to constant weight at 110° C., 16.53% of the material being due to NO_3.

The base diphenyl-endo-anilo-hydro-triazole (nitron) also precipitates the following acids: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydroferro- and hydroferricyanic, oxalic, picric and thiocyanic acids. Hence these must be absent from the solution if precipitation of nitric acid is desired for quantitative estimation.

Removal of Nitrous Acid. Finely powdered hydrazine sulphate is dropped into the concentrated solution. (0.2 gram substance per 5 or 6 cc.)

Chromic acid is reduced by addition of hydrazine sulphate.

Hydrobromic acid is decomposed by chlorine water added drop by drop to the neutral solution, which is then boiled until the yellow color has disappeared.

Hydriodic acid is removed by adding an excess of potassium iodate to the neutral solution and boiling until the iodine is expelled.

PROCEDURES FOR THE DETERMINATION OF COMBINED NITROGEN

Ammonia

The volumetric procedures for determination of ammonia are preferred to the gravimetric on account of their accuracy and general applicability. The following gravimetric method may occasionally be of use:

Gravimetric Determination of Ammonia by Precipitation as Ammonium Platinochloride, $(NH_4)_2PtCl_6$

Ammonia in ammonium chloride may be determined gravimetrically by precipitation with chlorplatinic acid. The method is the reciprocal of the one for determining platinum.

Procedure. The aqueous solution of the ammonium salt is treated with an excess of chlorplatinic acid and evaporated on the steam bath to dryness. The residue is taken up with absolute alcohol, filtered through a weighed Gooch crucible, and washed with alcohol. The residue may now be dried at 130° C. and weighed as $(NH_4)_2PtCl_6$, or it may be gently ignited in the covered crucible until

[1] Keep nitron reagent in a dark-colored bottle. M. Busch, Ber., **38**, 861 (1905). A. Gutbier, Z. Angew. Chem., 494, 1905.

ammonium chloride has been largely expelled and then more strongly with free access of air. The residue of metallic platinum is weighed. If the ignition method is to be followed, the ammonium platinic chloride may be filtered into a small filter, the paper with the washed precipitate placed in a porcelain crucible and then gently heated until the paper is charred (crucible being covered) and then more strongly with free access of air until the carbon has been destroyed.

Factors.[1] $(NH_4)_2PtCl_6 \times 0.2400 = NH_4Cl$, or $0.08095 = NH_4$, or $\times 0.0767 = NH_3$. $Pt \times 0.5453 = NH_4Cl$, or $\times 0.1839 = NH_4$, or $\times 0.1736 = NH_3$.

VOLUMETRIC METHODS FOR DETERMINATION OF AMMONIA

Two conditions are considered:

A. Estimation of free ammonia in solution.

B. Determination of ammonia in its salts—combined ammonia.

Analysis of Aqua Ammonia

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl orange or methyl red as indicator.

Procedure. About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800-cc. Erlenmeyer flask containing about 200 cc. of water and sufficient $\frac{1}{2}$ normal sulphuric acid to combine with the ammonia and about 10 cc. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

One cc. $\frac{1}{2}$ N. $H_2SO_4 = 0.0085$ gram NH_3.

Factor. $H_2SO_4 \times 0.3473 = NH_3$.

NOTE. The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in strong ammoniacal solutions.

Determination of Combined Ammonia. Ammonium Salts.

Strong bases decompose ammonium salts, liberating ammonia. This may be distilled into standard acid or into a saturated solution of boric acid (neutral to methyl orange) and titrated.

Procedure. About 1 gram of the substance is placed in a distillation flask (see Fig. 50) and excess of sodium or potassium hydroxide added and the ammonia distilled into a saturated solution of boric acid or an excess of standard sulphuric acid. Ammonia in boric acid solution may be titrated directly with standard acid (methyl orange or methyl red indicator) or in case a mineral acid

[1] Factors recommended by Treadwell and Hall, "Analytical Chemistry," 2, John Wiley & Sons.

was used to absorb the ammonia, the excess of acid is titrated with standard caustic solution.

One cc. half normal sulphuric acid = 0.0085 gram NH_3.

One cc. normal acid = 0.01703 gram NH_3.

Factors. $H_2SO_4 \times 0.3473 = NH_3$ and $NH_3 \times 2.8792 = H_2SO_4$.

ANALYSIS OF AMMONIACAL LIQUOR

The crude liquor by-product from coal gas in addition to ammonia contains hydrogen sulphide, carbon dioxide, hydrochloric acid, sulphuric acid, combined with ammonia, also sulphites, thiosulphates, thiocyanates, cyanides, ferrocyanides, phenols.

Determination of Ammonia

Volatile Ammonia. This is determined by distillation of the ammonia into an excess of standard sulphuric acid and titrating the excess of acid. With the exception that caustic soda is omitted in this determination, the details are the same as those for total ammonia as stated in the next paragraph.

Total Ammonia. The true value of the liquor is ascertained by its total ammonia content. Ten to 25 cc. of the sample is diluted to about 250 cc. in a distilling flask with a potash connecting bulb, as previously described, 20 cc. of 5% sodium hydroxide are added and about 150 cc. of solution distilled into an excess of sulphuric acid. The excess is then titrated according to the standard procedure for ammonia.

One cc. N. H_2SO_4 = 0.01703 gram NH_3.

Fixed Ammonia is the difference between the total and the volatile ammonia.

Carbon Dioxide

Ten cc. of the liquor are diluted to 400 cc. and 10 cc. of 10% ammoniacal calcium chloride added and the mixture, placed in a flask with Bunsen valve, is digested on the water bath for two hours. The precipitated calcium carbonate is washed, placed in a flask and an excess of N/2 HCl added and the excess acid titrated with N/2 NaOH.

N/2 HCl = 0.011 gram CO_2.

Hydrochloric Acid

Ten cc. of the liquor is diluted to 150 cc. and boiled to remove ammonia. Now hydrogen peroxide is added to oxidize organic matter, etc., the mixture being boiled to remove the excess of the peroxide. Chlorine is titrated in presence of potassium chromate as indicator by tenth normal silver nitrate after neutralizing with dilute nitric acid.

One cc. N/10 $AgNO_3$ = 0.00364 gram HCl.

Hydrogen Sulphide

To 10 cc. of the liquor are added an excess of ammoniacal zinc chloride or acetate, the mixture diluted to about 80 cc. and warmed to 40°. After settling for half an hour the zinc sulphide is filtered off and washed with warm water (40 to 50°); the precipitate is washed from the filter into an excess of N/10 iodine solution, the sulphide clinging to the paper washed into the main solution with hydrochloric acid. The mixture is acidified and the excess iodine titrated with N/10 sodium thiosulphate.

One cc. N/10 I = 0.0017 gram H_2S or 0.0016 gram S.

Sulphuric Acid

250 cc. of the liquor is concentrated to 10 cc., 2 cc. of concentrated hydrochloric added and the mixture heated to decompose any thiosulphate, sulphide or sulphite present. The concentrate is extracted with water, filtered and made to 250 cc. The sulphuric acid is now precipitated in an aliquot portion with barium chloride.

$BaSO_4 \times 0.4202 = H_2SO_4$, or $\times 0.1374$ = S present as H_2SO_4.

Total Sulphur. Fifty cc. of the liquor is run by means of a pipette into a deep beaker (250 cc. capacity), containing an excess of bromine covered by dilute hydrochloric acid. The mixture is evaporated to dryness on the steam bath and the residue taken up with water and diluted to 250 cc. Sulphur is now precipitated as barium sulphate as usual, preferably on an aliquot portion.

For a more complete analysis of crude liquor determining sulphite, thiosulphate, thiocyanate, hydrocyanic acid, ferrocyanic acid, and phenols the analyst is referred to Lunge, "Technical Methods of Chemical Analysis," Part II, Vol. II, D. Van Nostrand Co.

Determination of Traces of Ammonia

The determination of traces of ammonia is best accomplished by the colorimetric method with Nessler's reagent. Details of the procedure are given in the chapter on water analysis.

NITRIC ACID. NITRATES

The alkalimetric method for determining free nitric acid, and the complete analysis of the commercial product are given in the chapter on Acids. Special procedures for determining the combined acid are herein given.

Gravimetric Method for Determining Nitric Acid by Precipitation as Nitron Nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$

As in case of ammonia the volumetric methods are generally preferable for determining nitric acid, combined or free. Isolation of nitric acid by precipitation as nitron nitrate may occasionally be used. The fairly insoluble, crystalline compound, $C_{20}H_{16}N_4 \cdot HNO_3$ is formed by addition of the base diphenyl-endo-

anilo-hydro-triazole (nitron) to the solution containing the nitrate as directed under Separations. The precipitate washed with ice-water is dried to constant weight at 110° C. 16.53% of the compound is NO_3.

NOTE. The following acids should not be present in the solution, since their nitron salts are not readily soluble: nitrous, chromic, chloric, perchloric, hydrobromic, hydroiodic, hydroferrocyanic, hydroferricyanic, oxalic, picric and thiocyanic acids.

Solubility of less soluble nitron salts in 100 cc. of water. Nitron nitrate = 0.0099 gram, nitron bromide = 0.61 gram, iodide = 0.017 gram, nitrite = 0.19 gram, chromate = 0.06 gram, chlorate 0.12 gram, perchlorate = 0.008 gram, thiocyanate = 0.04 gram. (Treadwell and Hall, "Analytical Chemistry, Quantitative Analysis.")

VOLUMETRIC METHODS

Direct Estimation of Nitrates by Reduction to Ammonia. Modified Devarda Method [1]

An accurate procedure for the determination of nitrogen in nitrates is Allen's modification of the Devarda method. The method is based upon the quantitative reduction of nitrates to ammonia in an alkaline solution by an alloy consisting of 45 parts of aluminum, 50 parts of copper and 5 parts of zinc. The ammonia evolved is distilled into standard sulphuric acid and thus estimated. The method, originally designed for the valuation of sodium or potassium nitrates, is also of value in the determination of nitric acid, nitrites or ammonia. In the latter case the alloy is omitted.

Reagents Required. ***Devarda's Alloy.*** Forty-five parts aluminum, 50 parts copper and 5 parts zinc. The aluminum is heated in a Hessian crucible in a furnace until the aluminum begins to melt, copper is now added in small portions until liquefied and zinc now plunged into the molten mass. The mix is heated for a few moments, covered and then stirred with an iron rod, allowed to cool slowly with the cover on and the crystallized mass pulverized.

Standard Sulphuric Acid. This is made from the stock C.P. acid by dilution so that 1 cc. is equal to 0.0057 gram H_2SO_4, 100 cc. of acid of this strength being equivalent to approximately 1 gram of sodium nitrate. (A tenth normal acid will do, a smaller sample being taken for analysis.) Since it is necessary to standardize this acid against a standard nitrate, it is advisable to have an acid especially for this determination rather than a common reagent for general use.

Standardization of the Acid. 11.6 grams of standard potassium nitrate, equivalent to about 9.6 grams of $NaNO_3$, is dissolved and made to volume in the weighing bottle (100 cc.), and 10 cc. is placed in the Devarda flask, reduced and the ammonia distilled into 100 cc. of the acid, exactly as the following method describes. The temperature of the acid is noted and its value in terms of H_2SO_4, KNO_3 and $NaNO_3$ stated on the container. The acid expands or contracts 0.029 cc. for every degree centigrade above or below the temperature of standardization.

Standard Potassium Nitrate. The purest nitrate that can be obtained is recrystallized in small crystals, by stirring, during the cooling of the supersaturated concentrated solution, and dried first at 100° C. for several hours and then

[1] Paper by W. S. Allen, General Chemical Company, Eighth International Congress of Applied Chemistry.

at 210° C. to constant weight. Chlorides, sulphates, carbonates, lime, magnesia and sodium are tested for and if present are determined and allowance made.

Standard Sodium Hydroxide. This should be made of such strength that 1 cc. is equal to 1 cc. of the standard acid, 2 cc. methyl red being used as indicator. Ten cc. of the acid are diluted to 500 cc. and the alkali added until the color of the indicator changes from a red to a straw color.

Methyl Red Solution. 0.25 gram of methyl red is dissolved in 2000 cc. of 95% alcohol; 2 cc. of the indicator is used for each titration. As the indicator is sensitive to CO_2, all water used must first be boiled to expel carbonic acid. (Baker & Adamson, manufacturers of methyl red.)

Sodium Hydroxide—Sp.gr. 1.3. Pure sodium hydroxide is dissolved in distilled water and boiled in an uncovered casserole with about 1 gram of Devarda's alloy to remove ammonia. This is cooled and kept in a well-stoppered bottle.

Apparatus. This is shown in the accompanying illustration, Fig. 51. It consists of the Devarda flask connected to the scrubber *K*, filled with glass wool. This

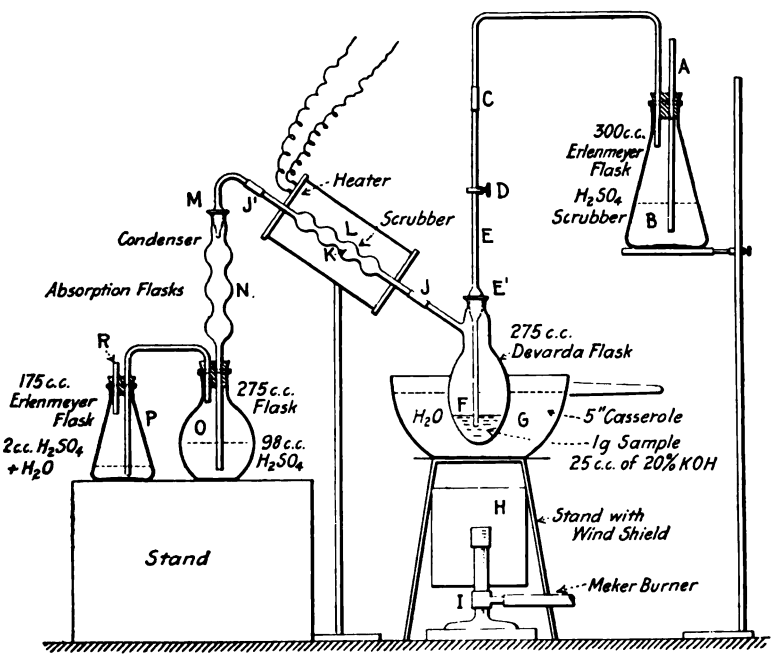


FIG. 51.—Devarda's Apparatus.

scrubber is heated by an electric coil or by steam passed into the surrounding jacket. The scrubber prevents caustic spray from being carried over into the receiving flask *O*. The form of the apparatus can best be ascertained from the sketch.

Weighing bottle with graduation at 100 cc. and a 10-cc. dropper with rubber bulb is used for weighing out the sample in solution. See Fig. 52.

Preparation of the Sample

Weight. It is advisable to take a large sample if possible, e.g., 100 grams of $NaNO_3$, 119 grams of KNO_3 or about 80 grams of strong HNO_3 (95%) or more if the acid is dilute. Solids are taken from a large sample, all lumps being broken down. After dissolving in water the sample is made up to 1 liter. (Scum is broken up by addition of a little alcohol.) One hundred cc. of this solution is placed in the weighing bottle, which has been previously weighed, being perfectly clean and dry. The difference is the weight of the 100-cc. sample.

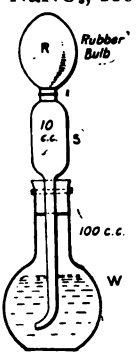


FIG. 52. Weighing Bottle and Dropper.

Manipulation. All parts of the apparatus are washed out with CO_2-free water. All water used in this determination should be boiled to expel CO_2. Ninety-eight cc. of the standard acid is placed in flask *O* and washed down with 2 to 3 cc. of water. Two cc. of the standard acid is placed in flask *P* and washed down with 10 cc. of water and 13 to 14 drops of methyl red indicator added. Connections are made between the flasks and the scrubber. (The correction is made for the acid, the temperature being noted at the time of withdrawal.) A casserole, filled with cold water, is placed under *F* (see illustration). The stem *E* is removed from the Devarda flask and 10 cc. (or more) of the nitrate added by means of the dropper in the weighing bottle, a funnel having been inserted in the flask. The bottle reweighed gives the weight of the sample removed, by difference. The nitrate is washed down with 10 cc. of water and 25 cc. of 20% caustic added (free from NH_3), the alkali washed down with 10 cc. more of water and then 3 grams of Devarda alloy placed in the flask by means of dry funnel. The stem *E* is quickly replaced, the stopcock being turned to close the tube. The reaction begins very soon. If it becomes violent, the reaction may be abated by stirring the water in the casserole, thus cooling the sample. After the energetic action has abated (five minutes), the casserole with the cold water is removed and the action allowed to continue for twenty minutes, meantime heat or steam is turned on in the scrubber. *E* is connected at *C* to the flask *B* containing caustic to act as a scrubber. It is advisable to have a second flask containing sulphuric acid attached to the caustic to prevent ammonia from the laboratory entering the system. A casserole with hot water is placed under *F* and the burner lighted and turned on full. A gentle suction is now applied at *R*, the stop-cock *D* being turned to admit pure air into the evolution flask; the rate should be about 5 to 6 bubbles per second. The suction is continued for thirty minutes, hot water being replaced in the casserole as the water evaporates. The heat is now turned off and the apparatus disconnected at *M* and *J*. The contents of this elbow and the condenser are washed into the flask *O*. The acid in *O* and *P* poured into an 800-cc. beaker and rinsed out several times. The volume in the beaker is made up to 500 cc., 1 cc. of methyl red added, and the free acid titrated with the standard caustic. The end-point is a straw yellow.

Calculation. The cc. of the back titration with caustic being deducted, of the acid remaining (e.g., combined with ammonia) is corrected to condition. Expansion or contraction of the acid is 0.029 cc. per each ove or below the temperature at which the acid was standardized. exactly 0.057 gram H_2SO_4 per cc., the result multiplied by 0.989 and

divided by the weight of the sample taken gives per cent nitrate. (In terms of $NaNO_3$.)

The Weight of the Sample. Ten times the difference of the weighings of the bottle *W* before and after removal of the 10 cc. and the product divided by the weight of the 100 cc. of the solution equals the weight of solid taken.

Example. *Weight* of the bottle + 100 cc. sample = 218 grams. Weight of the bottle = 112 grams, therefore weight of 100 cc. $NaNO_3$ = 106 grams.

Weight of the bottle + 100 cc. sample = 218. Weight after removal of 10 cc = 207.4 grams, therefore sample taken = 10.6 grams, including the added water. Now from above the weight of the actual sample taken = $10.6 \times 10 \div 106 = 1$ gram.

Temperature Correction. Temperature of standardization = 20° C. Temperature of the sulphuric acid when taken for the analysis = 31° C. Back titration of the caustic = 2 cc. The correct volume = $(100-2)-((31-20)\times 0.029) = 97.681$ cc. H_2SO_4 combined with ammonia from the reduced nitrate. $97.681 \times 0.989 \div 1 = 96.62\%$ $NaNO_3$.

Factors. $H_2SO_4 \times 2.06107 = KNO_3$ or $\times 1.7334 = NaNO_3$ or $\times 1.2850 = HNO_3$.

$H_2SO_4 \times 0.9587 = HNO_3$ or $\times 0.3473 = NH_3$.

$NH_3 \times 3.6995 = HNO_3$ or $\times 4.9906 = NaNO_3$ or $\times 4.0513 = NaNO_3$.

$NaNO_3 \times 1.1894 = KNO_3$ and $KNO_3 \times 0.8408 = NaNO_3$.

ANALYSIS OF NITRATE OF SODA

The following impurities may occur in nitrate of soda: KNO_3, NaCl, Na_2SO_4, Na_2CO_3, $NaClO_3$, $NaClO_4$, Fe_2O_3, Al_2O_3, CaO, MgO, SiO_2, H_2O, etc. In the analysis of sodium nitrate for determination of $NaNO_3$ by difference, moisture, NaCl, Na_2SO_4 and insoluble matter are determined and their sum deducted from 100, the difference being taken as $NaNO_3$. Such a procedure is far from accurate, the only reliable method being a direct determination of niter by the Devarda method given in detail. The following analysis may be required in the valuation of the nitrate of soda.

Determination of Moisture

Twenty grams of sample are heated in a weighed platinum dish at 205 to 210° C. for fifteen minutes in an air bath or electric oven. The loss of weight multiplied by 5 = per cent moisture. (Save sample for further tests.)

Insoluble Matter

Ten grams are treated with 50 cc. of water and filtered through a tared Gooch. The increased weight dried residue (100° C.) multiplied by 10 = per cent insoluble matter. (Save filtrate.)

Sodium Sulphate

The moisture sample is dissolved in 20 cc. hot water and transferred to a porcelain crucible. It is evaporated several times with hydrochloric acid to dryness to expel nitric acid. (Until no odor of free chlorine is noticed when thus treated.) Fifty cc. of water and 5 cc. hydrochloric acid are now added and the

sample filtered. Any residue remaining is principally silica. The filtrate is heated to boiling, 10 cc. of 10% barium chloride solution added, and the precipitated sulphate filtered off, ignited and weighed.

$$BaSO_4 \times 3.0445 = \text{per cent } Na_2SO_4.$$

Iron, Alumina, Lime, and Magnesia

These impurities may be determined on a 20-gram dried sample, the material being dried and evaporated as in case of the sodium sulphate determination. The filtrate from silica is treated with ammonium hydroxide and $Fe(OH)_3$ and $Al(OH)_3$ filtered off. Lime is precipitated from the iron and alumina filtrate as oxalate and magnesia determined by precipitation as phosphate from the lime filtrate by the standard procedures.

Sodium Chloride

The filtrate from the insoluble residue is brought to boiling and magnesia, MgO (Cl free), is added until the solution is alkaline to litmus. 0.5 cc. of 1% potassium chromate (K_2CrO_4) solution is added as an indicator and then the solution is titrated with a standard solution of silver nitrate until a faint red tinge is seen, the procedure being similar to the determination of chlorides in water by silver nitrate titration. The cc. $AgNO_3 \times$ factor for this reagent $\times 10$ = per cent NaCl.

Silver nitrate is standardized against a salt solution.

Carbonates

This determination is seldom made. CO_2 may be tested for by addition of dilute sulphuric acid to the salt. Effervescence indicates carbonates. Any evolved gas may be tested by lime water, which becomes cloudy if CO_2 is present. For details of the procedure reference is made to the chapter on Carbon.

DETERMINATION OF NITRIC NITROGEN IN SOIL EXTRACTS

Vamari-Mitscherlich-Devarda Method

Procedure. Forty cc. of water, a small pinch of magnesia and one of magnesium sulphate are added to flask *D* of the Mitscherlich apparatus (Fig. 53). Twenty-five cc. of standard acid and 60 cc. of neutral redistilled water are placed in flask *F*; 250 or 300 cc. of aqueous soil extract are placed in a 500-cc. Kjeldahl flask, 2 cc. of 50% sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask boiled for thirty minutes. The water which has boiled off is replaced, and, after cooling, 1 gram of Devarda's alloy (60 mesh), and a small piece of paraffin are added and the flask connected with the apparatus; reduction and distillation are carried on for forty minutes. The receiver contents are then cooled, 4 drops of 0.02%

solution of methyl red added, the excess acid is nearly neutralized, the liquid boiled to expel CO_2, cooled to 10 to 15° and the titration completed.

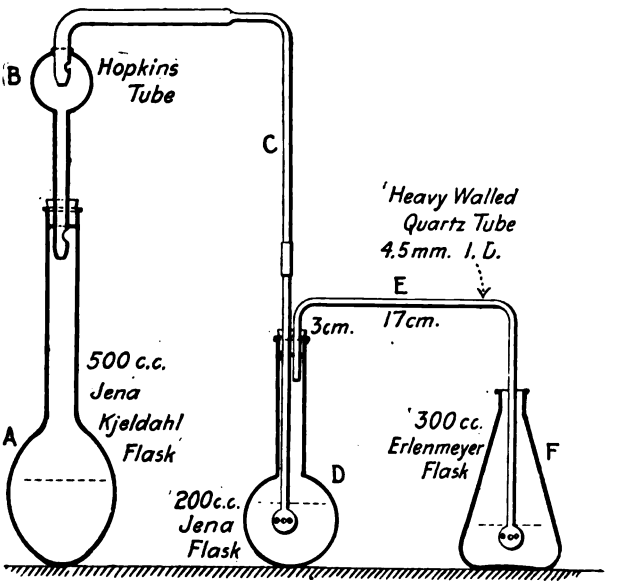


FIG. 53.—Mitscherlich's Apparatus for Nitrogen Determination.

DETERMINATION OF NITROGEN OF NITRATES (AND NITRITES) BY MEANS OF THE NITROMETER

The nitrometer is an exceedingly useful instrument employed in the accurate measurement of gases liberated in a great many reactions and has therefore a number of practical applications. It may be used in the determination of carbon dioxide in carbonates; the available oxygen in hydrogen dioxide; in the valuation of nitrous ether and nitrites; in the valuation of nitrates and nitric acid in mixed acids.

The method for the determination of nitrogen in nitrates, with which we are concerned in this chapter, depends on the reaction between sulphuric acid and nitrates in presence of mercury:

$$2KNO_3+4H_2SO_4+3Hg=K_2SO_4+3HgSO_4+4H_2O+2NO.$$

The simplest type of apparatus is shown in the illustration, Fig. 54. The graduated decomposition tube has a capacity of 100 cc. It is connected at the base by means of a heavy-walled rubber tubing with an ungraduated leveling tube (*b*). At the upper portion of (*a*) and separated from it by a glass stop-cock (*s*) is a bulb (*c*) of about 5 cc. capacity; a second stop-cock enables completely enclosing the sample, as may be necessary in volatile compounds. The glass stop-cock (*s*), directly above the graduated chamber, is perforated so as

to establish connection with the tube (*d*) when desired and the graduated cylinder (*a*).

Procedure. The tube (*b*) is filled with mercury and the air in (*a*) now displaced by mercury, by turning the stop-cock to form an open passage between (*a*) and (*d*) and then raising (*b*). A sample of not over 0.35 gram potassium nitrate or a corresponding amount of other nitrates, is introduced into (*c*), the material being washed in with the least amount of water necessary (1 to 2 cc.). By lowering (*b*) and opening the stop-cock *s* the solution is drawn into the decomposition chamber, taking care that no air enters. This is followed by about 15 cc. of pure, strong sulphuric acid through s_1 and *s*, avoiding admitting air as before. NO gas is liberated by the heat of reaction between the sulphuric acid and the water solution. When the reaction subsides, the tube (*a*) is shaken to mix the mercury with the liquor and the NO completely liberated. The gas is allowed to cool to room temperature and then measured, after raising or lowering (*b*) so that the column of mercury is the calculated excess of height above that in (*a*) in order to have the gas under atmospheric pressure. The excess of height is obtained by dividing the length of the acid layer in (*a*), in millimeters, by 7 and elevating the level of the mercury in (*b*) above that in (*a*) by this quotient; i.e., if the acid layer = 21 mm. the mercury in (*b*) would be 3 mm. above that in (*a*). The volume of gas is reduced to standard conditions by using the formula

$$V' = \frac{V(P-w)}{760(1+0.00367t)}.$$

V' = volume under standard conditions; V = observed volume; P = observed barometric pressure in mm.; w = tension of aqueous vapor at the observed temperature, expressed in millimeters; t = observed temperature.

One cc. gas = 4.62 milligrams of KNO_3, or 3.8 milligrams $NaNO_3$ or 2.816 milligrams HNO_3.

Du Pont Nitrometer Method [1]

The Du Pont nitrometer, Fig. 55, is the most accurate apparatus for the volumetric determination of nitrates. By use of this, direct readings in per cent may be obtained, without recourse to correction of the volume of gas to standard conditions and calculations such as are required with the ordinary nitrometers.

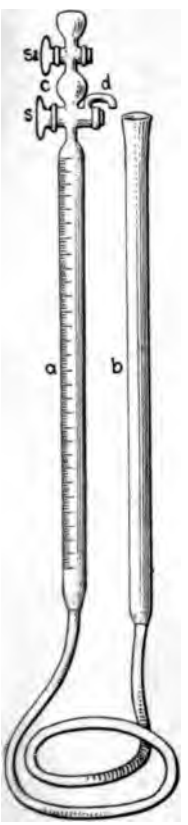
The apparatus consists of a generating bulb of 300 cc. capacity *E* with its reservoir *F* connected to it by a heavy-walled rubber tubing. *E* carries two glass stop-cocks as is shown in illustration. The upper is a two-way stop-cock connecting either the cup or an exit tube with the chamber. *D* is the chamber-reading burette, calibrated to read in percentages of nitrogen, and graduated from 10 to 14%, divided in 1/100%. Between 171.8 and 240.4 cc. of gas must be generated to obtain a reading. *A* is also a measuring burette, that may be used in place of *D* where a wider range of measurement is desired. "It is used for the measurement of small as well as large amounts of gas. It is most commonly graduated to hold 300.1 milligrams of NO at 20° C. and 760 mm. pressure and this volume is divided into 100 units (subdivided into tenths) each unit being equivalent to 3.001 milligrams of NO. When compensated, the gas from

[1] See paper by J. R. Pitman, Jour. Soc. Chem. Ind., p. 983, 1900.

imes the molecular weight in milligrams of any nitrate of the formula RNO_3 .ve times molecular weight of $R(NO_3)_2$) should exactly fill the burette. This lifies all calculations; for example the per cent nitric acid in a mixed acid d be

$$\frac{R63.02}{100W} = \text{per cent } HNO_3.$$

)urette reading, W = grams acid taken." [1] C is the compensating burette similar in form to the chamber burette D. B is the leveling bulb, by the



g. 54.—Nitrometer.

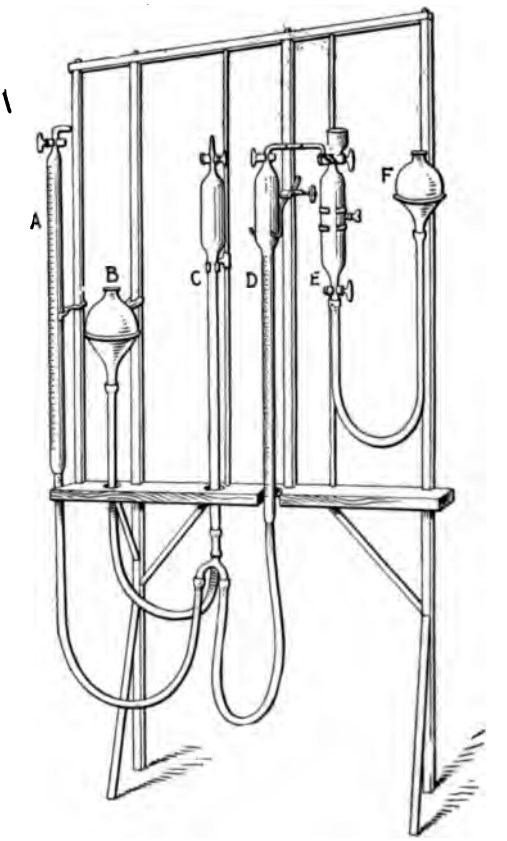


FIG. 55.—Du Pont's Nitrometer.

ıg or lowering of which the standard pressure in the system may be obtained. ıpparatus as shown in Fig. 55 is mounted on an iron stand. As in the more le form of apparatus, previously described, mercury is used as the con- ; liquid. The parts are connected by heavy-walled rubber tubing, wired e glass parts.

. W. Betts, Chemist, E. I. DuPont de Nemours Powder Co., in letter to author.

Standardizing the Apparatus. The apparatus having been arranged and the various parts filled with mercury, the instrument is standardized as follows: 20 to 30 cc. of sulphuric acid are drawn into the generating bulb through the cup at the top, and at the same time about 210 cc. of air; the cocks are then closed, and the bulb well shaken; this thoroughly desiccates the air, which is then run over into the compensating burette until the mercury is about on a level with the 12.30% mark on the other burette, the two being held in the same relative position, after which the compensating burette is sealed off at the top. A further quantity of air is desiccated in the same manner and run into the reading burette so as to fill up to about the same mark; the cocks are then closed, and a small piece of glass tubing bent in the form of a U, half filled with sulphuric acid (not water), is attached to the outlet of the reading burette; when the mercury columns are balanced and the enclosed air cooled down, the cock is again carefully opened, and when the sulphuric balances in the U-tube, and the mercury columns in both burettes are at the same level, then the air in each one is under the same conditions of temperature and pressure. A reading is now made from the burette, and the barometric pressure and temperature carefully noted, using the formula

$$V_t = \frac{V_o P_o (273+t)}{P_t 273},$$

the volume this enclosed air would occupy at 29.92 ins. pressure and 20° C. is found. The cock is again closed and the reservoir manipulated so as to bring the mercury in both burettes to the same level, and in the reading burette to the calculated value as well. A strip of paper is now pasted on the compensating burette at the level of the mercury, and the standardization is then complete.

Another rapid method of standardizing is to fill the compensating chamber with desiccated air as stated in the first procedure and then to introduce into the generating chamber 1 gram of pure potassium nitrate dissolved in 2 to 4 cc. of water, the cup is rinsed out with 20 cc. of 66° Béaume sulphuric acid, making three or four washings of it, each lot being drawn down separately into the bulb. The generated gas formed after vigorous shaking of the mixture, as stated under procedure, is run into the measuring burette. The columns in both burettes are balanced so that the reading burette is at 13.85 (=per cent N in KNO_3). A strip of paper is pasted on the compensating burette at the level of the mercury, and standardization is accomplished. By this method the temperature and pressure readings, and the calculations are avoided.[1]

Procedure for Making the Test. ***Salts.*** One gram of sodium or potassium nitrate, or such an amount of the material as will generate between 172 to 240 cc. of gas, is dissolved in a little water and placed in the cup of the generating bulb.

Liquid Acids. The acid is weighed in a Lunge pipette and the desired amount run into the funnel of the generating bulb, the amount of acid that is taken being governed by its nitrogen content.

The sample is drawn into the bulb; the funnel is then rinsed out with three or four successive washings of 95% sulphuric acid, the total quantity being 20 cc.

To generate the gas, the bulb is shaken well until apparently all the gas is

[1] Standardization with "C. P. KNO_3 is the better, as it is less tedious and is not subject to the correction errors that cannot be escaped when standardizing with air. The KNO_3 must be of undoubted purity."—A. W. Betts.

formed, taking care that the lower stop-cock has been left open, this cock is then closed and the shaking repeated for two minutes. The reservoir is then lowered until about 60 cc. of mercury and 20 cc. of acid are left in the generating bulb. There will remain then sufficient space for 220 cc. of gas.

NOTE. If too much mercury is left in the bulb, the mixture will be so thick that it will be found difficult to complete the reaction, a long time will be required for the residue to settle and some of the gas is liable to be held in suspension by the mercury, so that inaccurate results follow.

The generated gas is now transferred to the reading burette, and after waiting a couple of minutes to allow for cooling, both burettes are balanced, so that in the compensating tube the mercury column is on a level with the paper mark as well as with the column in the reading burette; the reading is then taken.

If exactly one gram of the substance is taken the percentage of nitrogen may be read directly, but in case of other amounts being taken, as will invariably be the case in the analysis of acids, the readings are divided by the weight of the substance and multiplied by 4.5 to obtain the per cent of nitric acid monohydrate present.

The procedure may be used for determining nitrites as well as nitrates.

Determination of HNO_3 in Oleum by Du Pont Nitrometer Method [1]

About 10 cc. oleum are weighed in a 30-cc. weighing bottle, 10 cc. 95% reagent sulphuric acid added and mixed by shaking. This mixture is transferred to the nitrometer reaction tube and the weighing bottle and nitrometer cup rinsed with three 5-cc. portions of the reagent sulphuric acid which is drawn into the reaction tube. This is vigorously shaken for three minutes and the gas then passed to the measuring tube and allowed to stand for about five minutes, after which the mercury levels are adjusted and the reading taken.

It is obvious that this determination includes any nitrous acid in the oleum.

Combined Nitric Acid

The nitric acid in nitrates may be determined by titration with ferrous sulphate. The nitrate dissolved in a little water is run into strong sulphuric acid and titrated with standard ferrous sulphate according to the procedure described for determining free nitric acid in mixed acids in the chapter on the subject.

[1] By courtesy of E. I. du Pont de Nemours Powder Co.

PHOSPHORUS

WILFRED W. SCOTT

P_4, *at.wt.*31.04; *sp.gr.* { *yellow* 1.831 / *red* 2.296; *m.p.* { 44° / 725°; *b.p.* { 290°C / .....; *oxides*, P_2O_3, PO_2, P_2O_5; *acids*, H_3PO_2, H_3PO_3, H_3PO_4, HPO_3, $H_4P_2O_7$.

DETECTION

Element. Phosphorus is recognized by its glowing (phosphorescence) in the air. The element is quickly oxidized to P_2O_5; if the yellow modification is slightly warm (34° C.) the oxidation takes place with such energy that the substance bursts into flame. The red form is more stable. It ignites at 260° C.

Boiled with KOH or NaOH it forms phosphine, PH_3, which in presence of accompanying impurities is inflammable in the air.

Phosphorus oxidized to P_2O_5 may be detected with ammonium molybdate, a yellow compound, $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 3H_2O$, being formed.

Acids. ***Hypophosphorous Acid, H_3PO_2,*** heated with copper sulphate to 55° C. gives a reddish-black compound, Cu_2H_2, which breaks down at 100° to H and Cu. Permanganates are reduced immediately by hypophosphorous acid. No precipitates are formed with barium, strontium or calcium solutions. Zinc in presence of sulphuric acid reduces hypophosphorous acid to phosphine, PH_3.

Phosphorous Acid, H_3PO_3. Copper sulphate is reduced to metallic copper and hydrogen is evolved, no Cu_2H_2 being formed as in case of hypophosphorous acid. Permanganates are reduced slowly. Added to solutions of barium, strontium or calcium white phosphites of these elements are precipitated. Alkali phosphites are soluble in water, while hypophosphites are not readily soluble.

Orthophosphoric Acid, H_3PO_4. Ammonium phosphomolybdate precipitates yellow ammonium phosphomolybdate from slightly nitric acid solutions. The precipitate is soluble in ammonium hydroxide.

Metaphosphoric Acid, HPO_3. Converted by nitric acid in hot solutions to the ortho form. Metaphosphoric acid is not precipitated by ammonium molybdate.

Pyrophosphoric Acid, $H_4P_2O_7$. Converted to orthophosphoric acid in hot solutions by nitric acid. No precipitate is formed with ammonium molybdate.

COMPARISON OF ORTHO, META AND PYROPHOSPHORIC ACIDS

Reagent.	Orthophosphoric acid.	Metaphosphoric acid.	Pyrophosphoric acid.
Ammonium molybdate	Yellow ppt.	No ppt.	No ppt.
Albumin	.....	Coagulated	Not coagulated
Zinc sulphate, cold, in excess	.....	No ppt.	White ppt.
Silver nitrate in neutral solution	Yellow ppt., Ag_3PO_4	White ppt., $AgPO_3$	White ppt., $Ag_4P_2O_7$
Magnesium salts	White ppt.	No ppt.	No ppt.

Phosphorous acids are distinguished from phosphoric acids by the phosphine ormed with the former when acted upon with zinc.

Acid phosphates are distinguished from normal phosphates as follows: Neutral silver nitrate added to an acid phosphate liberates free nitric acid (Litmus est), the following reaction taking place:

$$3AgNO_3+Na_2HPO_4=Ag_3PO_4+2NaNO_3+HNO_3.$$

The solution resulting when silver nitrate is added to normal phosphate solution is neutral.

$$3AgNO_3+Na_2PO_4=Ag_3PO_4+3NaNO_3.$$

ESTIMATION

The determination of the pentoxide of phosphorus is required in a large number of substances, since it is widely distributed in the form of phosphates—calcium phosphate, $Ca_3(PO_4)_2$; fluor apatite, $3Ca_3(PO_4)_2\cdot CaF_2$; chlor apatite, $3Ca_3(PO_4)_2\cdot CaCl_2$; vivianite, $Fe_3(PO_4)_2\cdot 8H_2O$; wavelite, $2Al_2(PO_4)_2\cdot Al_2(OH)_6\cdot 9H_2O$; pyromorphite, $3Pb_3(PO_4)_2\cdot PbCl_2$; phosphates of iron and calcium in phosphate ores, hence in slags of the blast furnace. It occurs in fertile soils, bones, plant and animal tissues.

The chemist is especially concerned in the determination of phosphoric acid (P_2O_5), in the evaluation of materials used for the manufacture of the acid—bone ash and phosphate rock (see table below). Generally, determinations of lime, iron and alumina are also desired and frequently a more complete analysis. In the analysis of phosphoric acid certain impurities occurring in the crude material used are determined, e.g., iron, lime, magnesia, sulphuric, hydrochloric and hydrofluoric acids, etc. Phosphoric acid is determined in the evaluation of phosphate fertilizers, phosphates used in medicine, phosphate baking powders, etc.

The element is determined in iron, steel, phosphor bronzes, and other alloys.

TYPICAL ANALYSES *

Substance.	Bone Ash.	Charlestown Phosphate.	Spanish Phosphorite.	Sombrero Phosphate.	Redonda Phosphates.	Canadian Phosphate.
Phosphoric oxide	39.55	27.17	33.38	35.12	35.47	37.68
Sulphur trioxide	.....	3.30	0.57			
Carbon dioxide	4.43–	4.96	4.10	7.40		
Lime	52.46	44.03	47.16	51.33	.....	51.04
Magnesia	1.02	0.37	trace			
Alumina	.....	1.44	0.89	+Fe	20.17	Fe_2O_3,
Ferric oxide	0.17	0.43	2.59	1.02	8.85	Al_2O_3,
Fluorine, etc	.....	2.38	4.01	.....	.....	F. etc.
Alkaline salts	.....	0.87	.....	0.42		=6.88
Silica—sand, etc	0.51	5.60	3.71	2.02	9.70	4.29

* Thorpe, " Dictionary of Applied Chemistry," Longmans, Green & Co.

Preliminary Remarks. Practically all procedures for the determination of phosphorus depend upon its oxidation to ortho phosphoric acid and its precipitation by ammonium molybdate from a nitric acid solution as ammonium phospho-molybdate. It may now be determined either gravimetrically or volumetrically. Two procedures are of importance in the gravimetric deter-

mination of phosphorus; the first depends upon the direct weighing of the yellow phosphomolybdate, dried at 110° C.; the second, on the conversion of the yellow precipitate to the magnesium salt and its ignition to pyrophosphate. Two volumetric procedures, which are of special value in the determination of small amounts of phosphorus as in case of phosphorus in iron and steel, are to be recommended for their rapidity and accuracy. One of these is to dissolve the ammonium phosphomolybdate in a known amount of standard caustic, titrate the excess of alkali with standard acid, which indicates the alkali required to neutralize the molybdic acid in the yellow precipitate. From this the amount of phosphorus present may be calculated. A second procedure of equal accuracy and rapidity is to dissolve the molybdate in ammonia, add an excess of sulphuric acid, pass the warm solution through a column of zinc and titrate the reduced molybdic acid with standard potassium permanganate, the amount of permanganate required being a measure of the phosphorus present.

The impurities interfering in the procedures are silica and arsenic acid. The first may be eliminated by dehydration of the silicic acid in the solution and its removal as insoluble SiO_2 by filtration. Arsenic in small quantities does not interfere under certain conditions; in large quantities its removal is imperative.

Preparation and Solution of the Sample

Amount of the Sample Required. For accurate results it is advisable to take a fairly large sample, 5 to 10 grams, and when it has been dissolved, to dilute to a definite volume, 500 or 1000 cc. Aliquots of this solution are taken for analysis.

Iron Ores, Phosphate Rock and Minerals. Five to 10 grams of the pulverized material placed in a 3-in. porcelain dish are digested for an hour with 50 to 100 cc. of concentrated hydrochloric acid (sp.gr. 1.19), the dish being covered by a clock-glass and placed on a steam bath. The acid is now diluted with half its volume of water and the solution filtered into a porcelain dish of sufficient capacity to hold the filtrate and washings. The residue is washed with dilute hydrochloric acid (1 : 1) until free of visible iron discoloration. The filtrate and washings are evaporated rapidly on a hot plate to small volume and then to dryness over the steam bath. Meanwhile the *insoluble residue* and filter are ignited in a 20-cc. platinum crucible over a Méker burner or in a muffle furnace and the residue fused with ten times its weight of sodium carbonate. The fusion is removed by inserting a platinum wire into the molten mass, allowing to cool and then gently heating until the mass loosens from the crucible, when it may be removed on the wire. The cooled mass on the wire and that remaining in the crucible are dissolved in dilute hydrochloric acid, and the filtered solution added to the main solution. The combined solutions are evaporated to dryness, and heated gently to dehydrate the silica. The residue is taken up with a few cc. of hydrochloric acid, the solution diluted, filtered and the SiO_2 washed with dilute nitric acid solution. The combined filtrates are made up to 500 or 1000 cc. Aliquots of this solution are taken for analysis.

Iron and Steel. Five to 10 grams of the drillings or filings are dissolved in an Erlenmeyer flask with 50 to 100 cc. of dilute nitric acid, 1 : 1, more acid being added if necessary. When dissolved, a strong solution of $KMnO_4$ is added until a pink color appears; on boiling brown manganese dioxide forms in the solution if a sufficient amount of permanganate has been added. This is dis-

lved by adding 2% sodium thiosulphate solution in just sufficient quantity to ssolve the precipitate. The solution is diluted to a convenient volume for alysis. Where a number of determinations are to be made, it is advisable weigh the amount of sample desired for the determination and to precipitate e ammonium phosphomolybdate in the flask in which the drillings have been ssolved.

Ores Containing Titanium. Titanium may be recognized by the red color roduced by hydrogen peroxide, H_2O_2, added to the sulphuric acid extract; also y the reduction test with zinc, which causes a play of colors, the solution becom- ng colorless by the reduction of iron, then, in presence of titanium, pink, purple nd finally blue. (Vanadium gives similar tests.) Solutions containing titanium requently appear milky when the solution is diluted before filtering off the insol- ble residue. Since titanium forms an insoluble compound with phosphoric acid nd iron oxide [1] the final residue, obtained by the method of solution for ores, phosphate rock and minerals, should be moistened with sulphuric acid and the silica expelled with hydrofluoric acid. The solution is evaporated to dryness and to SO_3 fumes, the residue fused with sodium carbonate and taken up with boiling water. TiO_2 remains insoluble, while P_2O_5 passes into the filtrate as the sodium salt. The procedure may be shortened by treating the original sample directly according to this method of solution, a 2-gram sample being taken, as larger amounts are difficult to handle.

Soluble Phosphates, Phosphate Baking Powder, etc. A water extract is generally sufficient to get the material in solution. In case iron, alumina, lime and magnesia salts are present, as may occur in baking powders, an extraction with dilute 3% nitric acid is necessary. It is advisable to dissolve a 5- to 10-gram sample and take an aliquot part of the solution made up to a definite volume. Before precipitating with ammonium phosphomolybdate, 5 grams of ammonium nitrate should be added for each gram of the sample taken for analysis and the solution boiled to oxidize compounds of phosphorus to the orthophosphate form.

Precipitation of Ammonium Phosphomolybdate

Precipitation of ammonium phosphomolybdate is common to all subsequent methods for determination of phosphorus, and, as in case of preparation and solution of the sample, details of this procedure will not be repeated.

Reaction.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

Special Reagents Required. ***Ammonium Molybdate.*** One hundred grams f pure molybdic acid are thoroughly mixed with 400 cc. of cold distilled water nd 80 cc. of strong ammonia (sp.gr. 0.90) added. When the solution is com- lete it is poured slowly and with constant stirring into a mixture of 400 cc. f strong nitric acid (sp.gr. 1.42) and 600 cc. distilled water. This order of rocedure should be followed, as the nitric acid poured into the ammonium olybdate solution will cause the precipitation of a difficultly soluble oxide of olybdenum and render the reagent practically worthless. Fifty milligrams 0.50 gram) of microcosmic salt, dissolved in a little water are added, the pre- ipitate agitated, then allowed to settle for twenty-four hours and the clear solu-

[1] Blair "Chemical Analysis of Iron."

tion decanted through a filter into a large reagent bottle. Sixty cc. of the reagent should be used for every 0.1 gram of P_2O_5 present in the solution analyzed.

Potassium Permanganate. For oxidation purposes. Two per cent solution filtered free of dioxide through asbestos is required.

Amount of Sample Required for Analysis. If the material contains over 20% P_2O_5, 0.1 to 0.5-gram sample should be taken; if the product contains 5 to 20% P_2O_5, 1.0 to 0.5 gram should be taken; for a sample containing 0. to 5%, 2.5 to 1-gram sample is taken, and for P_2O_5 less than 0.5%, a 5-gram sample is taken.

Precipitation. The free acid of the solution is nearly *neutralized* by *addition of ammonium hydroxide.* In analysis of phosphate rock or materials comparatively low in iron, it is advisable to add ammonium hydroxide in quantity sufficient to cause a slight permanent precipitate followed by just sufficient HNO_3 to dissolve the precipitate. In *iron and steel* analysis ammonium hydroxide is added until the precipitated iron hydroxide dissolves with difficulty and the solution becomes a deep amber color or cherry red. In analysis of *soluble phosphates,* litmus paper dropped into the solution indicates the neutral point. *Nitric acid* is added to the neutral or slightly acid solution, 5 cc. of acid for every 100 cc. of solution. A volume of 150 to 200 cc. of solution is the proper dilution for samples taken in amounts above recommended. To the warm solution (not over 80° C.) *ammonium molybdate is added,* 60 cc. of the reagent being required for every 0.1 gram of P_2O_5 present. The solution is stirred, or shaken, if in a flask, until a cloudy precipitate of ammonium phosphomolybdate appears. It is then allowed to settle on the steam bath at a temperature of 40 to 60° C., for one hour, then again agitated and allowed to settle in the cold for an hour longer. The filtrate should be tested with additional ammonium molybdate for phosphorus. The yellow precipitate is filtered and washed with 1% HNO_3 solution followed by a 1% solution of KNO_3, or NH_4NO_3 or $(NH_4)_2SO_4$ as the special case requires. Filtration through asbestos in a Gooch crucible is to be recommended. When a large number of determinations are to be made, as in case of iron and steel, filter paper is more convenient.

GRAVIMETRIC METHODS FOR DETERMINATION OF PHOSPHORUS

A. Direct Weighing of the Ammonium Phosphomolybdate

The sample being dissolved and the ammonium phosphomolybdate precipitated according to directions already given above, the supernatant solution is filtered through a weighed Gooch crucible and washed twice by decantation with dilute nitric acid (1%), the precipitate washed into the Gooch, followed by two washings with 1% KNO_3 or NH_4NO_3 (neutral solutions) and finally with water. The precipitate, free from contaminating impurities, is dried for two hours in a oven at 110° C., then cooled in a desiccator and weighed. Weight of precipitate $\times 0.0165 = P$, or $\times 0.03784 = P_2O_5$.

NOTE. If this procedure is to be followed it will be convenient to take 1.65 gram sample, if the phosphorus content will allow. Each 0.01 gram of precipitate will then equal 1% P.

B. Determination of Phosphorus as Magnesium Pyrophosphate

Magnesia Mixture. For precipitation of ammonium magnesium phosphate, 110 grams of magnesium chloride ($MgCl_2 \cdot 6H_2O$) are dissolved in a small amount of water. To this are added 280 grams of ammonium chloride and 700 cc. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 cc. with distilled water. The solution is allowed to stand several hours and then filtered into a large bottle with glass stopper. Ten cc. of the solution should be used for every 0.1 gram P_2O_5 present in the sample analyzed. As the reagent becomes old it will be necessary to filter off the silica that it gradually accumulates from the reagent bottle.

Procedure. The ammonium phosphomolybdate, obtained as directed (page 314), is filtered onto a 12½ S. & S. No. 589 filter paper and washed four or five times with dilute 1% HNO_3. The precipitate is now dissolved from the filter by a fine stream of hot ammonium hydroxide, 1 : 1, catching the solution in the beaker in which the precipitation was made. The solution and washings should be not over 100 to 150 cc. Hydrochloric acid is added to the cooled solution to neutralize the excess of ammonia, the yellow precipitate, that forms during the neutralization, dissolving with difficulty, when sufficient acid has been added. To the cooled solution *cold magnesia mixture is added* drop by drop (2 drops per second) with constant stirring. Ten cc. of the reagent will precipitate 0.1 gram P_2O_5. When the solution becomes cloudy the stirring is discontinued and the precipitate allowed to settle ten minutes. *Ammonium hydroxide is added* until the solution contains about one-fourth its original volume of strong ammonia (e.g. 25 cc. NH_4OH, 90 to 100 cc. of solution). The solution is stirred during the addition and then allowed to settle for at least two hours. It is filtered preferably, through a Gooch crucible (or through an ashless filter paper), and the precipitate washed with dilute ammonium hydroxide, 1 : 4, then placed in a porcelain crucible, a few drops of saturated solution of ammonium nitrate added and the precipitate heated over a low flame till decomposed (or until the paper chars). The lumps of residue are broken up with a platinum rod and again ignited over a Scimatico or Méker burner, the heat being gradually increased. If the heating is properly conducted, the resultant ash will be white or light gray, otherwise it will be dark. The addition of solid ammonium nitrate aids the oxidation in obstinate cases, but there is danger of slight mechanical loss. The crucible is cooled in a desiccator and the residue weighed as magnesium pyrophosphate.

$$Mg_2P_2O_7 \times 0.2787 = P \quad \text{and} \quad Mg_2P_2O_7 \times 0.6379 = P_2O_5.$$

Direct Precipitation of Magnesium Ammonium Phosphate

In the absence of heavy metals whose phosphates are insoluble in an ammoniacal solution, the magnesia mixture may be added directly to the neutral solution containing the phosphate, without previous precipitation of ammonium phosphomolybdate. The magnesium ammonium phosphate is washed and ignited according to directions given above, and weighed as magnesium pyrophosphate.

The use of the Gooch crucible for the ammonium phosphomolybdate and the ammonium magnesium phosphate precipitates is recommended in preference to filter paper, as the fibers of the latter invariably are occluded in the precipi-

tates, and produce dark-colored residues of magnesium pyrophosphate, which are, frequently, extremely difficult to burn white. The residue on the asbestos mat, on the other hand, is easily ignited white, and does not require repeated addition of an oxidizing agent, as is so often the case with precipitates filled with paper fiber.

VOLUMETRIC METHODS FOR THE DETERMINATION OF PHOSPHORUS

C. Alkalimetric Method

The method is based on the acid character of ammonium phosphomolybdate, the following reaction taking place with an alkali hydroxide:

$$2(NH_4)_3 12MoO_3PO_4 + 46NaOH + H_2O = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23H_2O.$$

From the reaction 46 molecules of sodium hydroxide are equivalent to one molecule of P_2O_5, hence 1 cc. of a N/10 solution of sodium hydroxide neutralizes the yellow precipitate containing an equivalent of .000309 gram of P_2O_5.

Special Reagents

Sodium Hydroxide—Tenth Normal Solution. For determination of phosphorus by the alkali volumetric method. To 100 grams of the pure NaOH sticks sufficient water is added to just dissolve the hydrate. This concentrated solution is poured into a tall cylinder, the vessel closed and the insoluble matter allowed to settle. The liquid will be practically free of carbonates. A portion of the clear liquor may now be drawn off and diluted to a definite volume so that the solution is slightly stronger than tenth normal, as determined by titration against a standard N/10 acid. It may now be diluted to the required amount as indicated by the acid titration. Freshly boiled distilled water should be used in the dilutions of the standard caustic solution. Phenolphthalein indicator is required in the titration. The exact value of the caustic solution in terms of phosphorus may be ascertained by standardizing the solution against a steel sample of known phosphorus content, the sample being dissolved in nitric acid, the phosphorus precipitated as ammonium phosphomolybdate, the washed precipitate dissolved by the caustic solution and the excess caustic titrated by standard nitric acid according to the procedure given later.

$$\frac{\text{Wt. of P in sample}}{\text{cc. of NaOH required to neutralize molybdate}} = \text{amount of P per cc. of NaOH.}$$

Nitric Acid—Tenth Normal Solution. The acid is standardized against the caustic solution and should be of such strength that 1 cc. of HNO_3 is equal to 1 cc. of NaOH. Phenolphthalein indicator is used. Approximately 6.7 cc. of 95% HNO_3 diluted to 1000 cc. = N/10 HNO_3 solution.

Nitric Acid for Washing Precipitates. One per cent solution, 14 cc. HNO_3 (sp.gr. 1.42) per liter of water.

Acid Ammonium Sulphate for Washing Precipitates. Fifteen cc. strong NH_4OH + 25 conc. H_2SO_4 in 1000 cc. solution.

Potassium Nitrate for Washing Precipitates. Used in volumetric analysis only. Ten grams of KNO_3 per liter of solution. Test, to be sure the solution is neutral.

Other reagents required: NH_4OH (sp.gr. 0.90); H_2SO_4 (sp.gr. 1.84); HNO_3 (sp.gr. 1.42); $Na_2S_2O_3$ solution, 2%; amalgamated zinc.

Special Apparatus Required

Jones' Reductor. Details of the reductor are given under the determination of iron by the permanganate method, also under the Volumetric Determination of Molybdenum, pages 220 and 281.

Procedure. The ammonium phosphomolybdate, obtained according to directions already given on page 313, is filtered into a Gooch crucible containing asbestos, and washed once or twice with water containing 1% nitric acid, and then several times with a 1% neutral solution of potassium nitrate until the washings are free of acid, as indicated by testing with litmus paper. The asbestos mat containing the precipitate is transferred to a No. 4 beaker, 100 cc. of CO_2 free water added, followed by about 20 cc. of N/10 NaOH measured from a burette. The crucible is rinsed out with 5 to 10 cc. of N/10 NaOH, the exact amount being noted and then with water, adding the rinsings to the main solution. Phenolphthalein indicator is added, and the excess of caustic titrated with N/10 HNO_3. The total NaOH added minus the acid titration equals the cc. of the caustic equired to react with the yellow precipitate.

One cc. N/10 NaOH = 0.000136 gram P and = 0.000309 gram P_2O_5.

The exact factor should be determined as directed under Reagents.

D. Zinc Reduction and Titration with Potassium Permanganate

This method is based on the assumption that ammonium phosphomolybdate, $(NH_4)_3 12MoO_3PO_4$, is reduced, in acid solution, by zinc, the molybdic acid, MoO_3, forming the lower oxide Mo_2O_3, in which form it reacts with ferric iron in the receiving flask, reducing a corresponding equivalent of ferric salt to ferrous condition, being itself oxidized to MoO_3.[1] When the ferric solution is not placed in the receiving flask a slight oxidation takes place, the oxide $Mo_{24}O_{37}$, apparently being formed.[2]

Potassium Permanganate Decinormal Solution. For volumetric determination of phosphorus, reduction method, 3.161 grams of the pure salt per liter is the theoretical amount required for a tenth-normal solution. It is necessary, however, to standardize the permanganate solution against a tenth-normal sodium oxalate solution. The exact value of the permanganate solution may be accurately and rapidly determined in terms of phosphorus by standardizing against a sample of standard steel containing a known amount of phosphorus, the ultimate standard being steel drillings furnished by the U. S. Bureau of Standards. The drillings are dissolved in nitric acid, oxidized with $KMnO_4$, the excess of the reagent being destroyed by thiosulphate solution. Ammonia is added until the solution becomes a deep amber color. The phosphorus is precipitated as ammonium phosphomolybdate. The following procedure is the same as is

[1] D. L. Randall, Am. Jour. Sci. (4), **24**, 315.
[2] Blair, "Chemical Analysis of Iron," 7th Ed., p. 96.

given in the volumetric method following: The permanganate titration of the reduced molybdic acid divided into the amount of phosphorus known to be present in the solution will give the value of the permanganate in terms of phosphorus.

$$\frac{\text{Wt. of P in sample}}{\text{cc. } KMnO_4 \text{ required}} = \text{amount of P per cc. of } KMnO_4.$$

Procedure. The ammonium phosphomolybdate, obtained by the procedure given on page 313, is filtered onto an asbestos mat in a Gooch crucible or onto filter paper, and washed with dilute HNO_3 followed by acid ammonium sulphate (15 cc. NH_4OH, sp.gr. 0.90+25 cc. conc. H_2SO_4, sp.gr. 1.84+1000 cc. H_2O), until 2 or 3 cc. of the wash water gives no reaction for molybdenum with a drop of ammonium sulphide solution. Five or six washings should suffice.

Reduction. The precipitate is dissolved by adding about 10 cc. ammonium hydroxide, sp.gr. 0.96, to the precipitate, catching the solution in the beaker or flask in which the precipitation was made. About 10 cc. of strong sulphuric acid is added to this solution after diluting to about 100 cc. The Jones reductor is prepared as described for determination of molybdenum by reduction, page 281. The receiving flask is charged with about 25 cc. of ferric alum (100 grams per liter) and 4 cc. syrupy phosphoric acid. In iron and steel analysis this mixture is omitted. One hundred cc. of hot water followed by 100 cc. of hot dilute sulphuric acid (2.50%) are passed through the column of zinc in the reductor (previously cleaned by passing hot dilute H_2SO_4 through it). The phosphomolybdic solution is now poured through the reductor, followed by 100 cc. 2% sulphuric acid and 100 cc. hot water. The solution as it is reduced becomes green, but upon coming in contact with the ferric solution produces a bright red color. In absence of ferric solution in the receiver the reduced solution appears green and should remain clear. The hot solution is titrated immediately with N/10 $KMnO_4$.

Titration. The reduced solution is poured into a No. 6 beaker and N/10 $KMnO_4$ added from a burette, until a faint permanent pink color is produced. During the titration, the solution changes in color to a brown, a pinkish yellow and finally to pink.

Titration of reduced ferric solution, 1 cc. N/10 $KMnO_4$ = 0.000862 P.

Titration in absence of ferric sulphate, 1 cc. N/10 $KMnO_4$ = 0.000887 P.

Calculation. Case 1. Ferric sulphate in the receiver ($6Mo_2O_3 + 18\,O = 12MoO_3$ in the molecule containing 1 P); 18 O are equivalent to 36 H, hence N/10 P according to this reaction equals at.wt. P divided by (36×1000) = P for 1 cc. N/10 $KMnO_4$ = 0.000862 g. P.

Case 2. No ferric salt in receiver. $Mo_{24}O_{37} + 35\,O = 24MoO_3 + 2P$. (35 O = 70 H). Dividing by 2 we get at.wt. P divided by (35×1000) = P for 1 cc. N/10 $KMnO_4$ = 0.000887.

Report of the Committee on Research and Analytical Methods—Phosphate Rock [1]

The following tentative standard methods for sampling and determination of moisture, phosphoric acid and iron and alumina in phosphate rock are recommended to the Division.

Methods of Sampling and Determination of Moisture

I. Gross Sample. *A. Car Shipments.* One hundred pounds sample per car.

1. *Sampling from the Car.* In sampling car shipments in the car at least ten scoopshovelsful, aggregating 100 lbs., shall be taken from each car at approximately equal distances from each other so as to average the car. Care shall be taken to see that each scoopful shall cover the entire face of the pile from floor to top.

2. *Sampling from the Cart or Barrow.* A small hand scoopful of 1 to 2 lbs. shall be taken from each cart or barrow either as it is being loaded or as it leaves the car.

B. Cargo Shipments. One hundred pounds minimum sample per vessel.

1. *Sampling in Hoisting Tub.* In sampling cargoes generally running from 1000 tons upward a small hand scoopful shall be taken from approximately every tenth tub before it is hoisted from the hold.

2. *Sampling from Conveyor.* If unloading is being done with automatic bucket and conveyor, periodical sections of the entire discharge of the conveyor shall be taken of such intervals and quantity as to give a sample equivalent to approximately 1 lb. per each 10 tons of cargo.

3. *Sampling from Conveying Vehicle.* Samples shall be taken with a hand scoop from various cars at such regular intervals and in such quantities as to give approximately 1 lb. for each 10 tons of cargo.

II. Laboratory Sample. The resulting gross sample obtained by any one of the methods outlined shall be crushed to pass a four-mesh screen, thoroughly mixed on a clean, hard surface and quartered down to a 10-lb. average sample.

A. Crushing. This 10-lb. sample shall all be crushed to pass an eight-mesh screen.

B. Mixing and Quartering. This eight-mesh sample shall be carefully mixed and quartered down to two 2-lb. samples.

C. Grinding. 1. *Moisture Sample.* One of these 2-lb. samples shall be held in an air-tight container. This sample is to be used for the determination of moisture.

2. *Analytical Sample.* The other 2-lb. sample shall be further mixed and quartered down to a 2- or 4-oz. sample which is then to be ground to pass a sixty-mesh screen or preferably a sixty-five mesh screen. This sample is to be used for the analytical determination.

NOTE. It is essential that the taking of the gross sample be done with small hand scoops and that the practice of taking the sample in the hand be absolutely prohibited, for it has been found that there is considerable selective action in the finer materials sifting through the fingers while a scoop retains the entire sample.

The dimensions of the screens referred to above are to be as follows:

No. of Mesh	Size of Opening Inches	Diameter of Wire Inches
4	0.185	0.065
8	0.093	0.032
65	0.0082	0.0072

III. Determination of Moisture. Moisture is to be determined on both the moisture sample and analytical sample. Of the moisture sample not less than 100 grams are to be weighed out for each determination. Of the analytical sample approximately 2 grams are to be weighed out for each determination. Both are to be dried to constant weight at a temperature of 105° C. in a well-ventilated oven, preferably with a current of dry air passing through the oven. The containers in which moisture is determined should be provided with well-fitting covers so that the samples may be cooled and weighed in the well-covered container.

[1] Journ. Ind. and Eng. Chem.

IV. Calculation of Results. The percentages of phosphoric acid and alumina as determined on the analytical sample are to be calculated to a free basis and subsequently to the basis of the original sample as shown by ure content of the moisture sample.

Determination of Phosphoric Acid

Reagents. To be prepared as in Official Methods, A. O. A. C. Bureau of Bulletin 107 (Rev.), 1910, p. 2. Preparation of reagents (*c*), (*d*), (*e*) and that the ammonium nitrate solution in (*d*) is changed to 5% instead of 10

Method of Solution. To 5 grams of the sample add 30 cc. of conc. h acid (sp.gr. 1.20) and 10 cc. of conc. nitric acid (sp.gr. 1.42) and boil syrupy consistency. The residue, which should be nearly solid after cooli up with 5 cc. of conc. nitric acid and 50 cc. of water. Heat to boiling and make up to 500 cc. through the filter. This procedure eliminates all of the silica and it is necessary to filter as quickly as possible after as to avoid redissolving the silica.

Determination. Draw off an aliquot portion of 50 cc., corresponding neutralize with ammonia, then add nitric acid until the solution is just 15 grams of ammonium nitrate (free from phosphates), heat the solut and add 150 cc. of molybdate solution. Digest at 50° C. for fifteen m frequent stirring. Filter off the supernatant liquid and test the filtrate date solution to see if precipitation has been complete. (If not, add mo to the filtrate and digest for fifteen minutes longer.) Wash with 5 per c nitrate solution by decantation, retaining as much of the precipitate as beaker. Dissolve the precipitate in the beaker in the least possible qua nium hydroxide (sp.gr. 0.90) and dilute this solution with several to of hot water. Dissolve the remainder of the precipitate on the filter tion, washing beaker and filter with hot water and keeping the volu between 75 and 100 cc. Neutralize with hydrochloric acid, cool to ture and add 25 cc. of magnesia mixture from a burette, drop b vigorously with a rubber-tipped rod, then add 15 cc. of ammonium h 0.90) and allow to stand for four hours or overnight at room temper of standing may be reduced to hours if kept in a refrigerator or ice-water bath. Filter thro platinum or porcelain Gooch cru a platinum or asbestos m lly made and ignited to consta with 2.5% ammonium until practically free from chlo cool and weigh as ma ophosphate. If desired, filtra through an ashless fil iting in the usual manner. multiplying by 0.63

Dete and Aluminum together as P

I. Solution hydrochloric acid (1 : 1); pre by volume of (sp. gr. 1.19) with 1 part of di ammonium chloride, which

ceriate, faintly acid (10%), prepa ral filtrate

nd correct result by the
uantity of HCl (diluted),
, cooling, adding 10 cc.

it is necessary first to
ess to eliminate chlorine,

808, and after deducting
the difference ($AlPO_4$)

Chainomatic Balance.

the usual construction of the analytical or
ings, etc., are concerned, with the exception
no graduations on the beam. One end of
m of the scale beam, and the other end from
down on a vertical graduated scale. As this
of the chain is taken from the beam and hangs
a stationary support for holding the inactive part
ered a greater proportion of the weight of the chain
means of this chain and vernier device, after all the
milligrams are placed on the pan, the weighing fro
am can be concluded without opening the balance
he necessity of reading and replacing all small weights
onsequent enormous saving of time. The editor has us
for over a year and has found it highly satisfactory.

is suitable), in a 3-in. rapid filtering funnel, keeping the contents of the beaker and funnel hot.[1] Wash three times with hot 5% ammonium nitrate solution, each time cutting the precipitate loose from the filter and stirring it thoroughly with the stream from the wash bottle and filling to within about ½ in. of its upper edge. About 30 cc. are required for each washing. Return the precipitate to the precipitating beaker by washing it out of the filter with a stream of hot water. Dissolve the precipitate with dilute HCl (1 : 6), pouring about 50 cc. through the filter in successive washings and using about 25 cc. to wash down inside the beaker. Finish filter paper with distilled water.

IV. Second Precipitation with Ammonium Acetate. Cool the solution to room temperature, add 50 cc. saturated ammonium chloride solution, 4 cc. of 10% ammonium phosphate solution, 2 drops of methyl orange, and adjust acidity as before. Dilute to 300 cc. with distilled water. Heat to boiling, add 15 cc. of 25% ammonium acetate solution and continue heating for about five minutes. Filter on the same paper as used for the first filtration, scrubbing the inside of the beaker with a rubber-tipped stirring rod and rinsing with hot 5% ammonium nitrate solution. Wash the precipitate ten times with hot 5% ammonium nitrate solution, each time cutting the precipitate loose, stirring it thoroughly as before and breaking up all lumps that it may contain. About 300 cc. of wash solution are required.

As a precautionary measure, boil the filtrate and washings from both the first and second precipitates, and recover any additional precipitate.

V. Ignition of Precipitate. Transfer filter with precipitate to a weighed deep-form porcelain crucible (40 mm. in diameter is a good size) and heat gently over a low flame until the contents are dry, increase the temperature a little and continue heating until the paper is charred, increase the temperature again and continue heating until the paper is entirely burned. Ignite the *uncovered*[2] porcelain crucible for one-hour periods over blast lamp No. 4 Méker burner to constant weight, each time cooling to room temperature in desiccator before weighing. Deduct the weight of blank from each determination, and after subtracting the weight of $FePO_4$ equivalent to the amount of iron found in 0.5 gram of rock by titration, calculate the remainder to Al_2O_3. $AlPO_4 \times 0.4184 = Al_2O_3$.

Determination of Iron

I. Solutions Required. 1. *Standard Potassium Permanganate*, N/40, containing 0.79015 gram of $KMnO_4$ per liter, and having a value of 0.001996 (or practically 0.002) gram of Fe_2O_3 per cc. Standardize with pure sodium oxalate (Bureau of Standards standard sample No. 40.)

2. *Stannous Chloride.* Dissolve 50 grams of the crystallized salt in 100 cc. of hot conc. HCl and make up to 1 liter with distilled water.

3. *Mercuric Chloride.* Prepare a cold saturated solution.

4. *Manganese Solution.* (Preventive solution): (*a*) Dissolve 200 grams of crystallized manganese sulphate in 1000 cc. of water. (*b*) Pour slowly, with constant stirring, 400 cc. of conc. sulphuric acid into 600 cc. of water and add 1000 cc. of phosphoric acid of 1.3 sp.gr. Mix solutions (*a*) and (*b*).

II. Analytical Procedure. Determine iron according to Jones' and Jeffrey's modification of the Zimmermann-Reinhardt method[3] as follows: Place in a 250-cc. beaker an aliquot of the rock solution, containing not more than 5 cc. of conc. HCl, boil and reduce with the smallest possible excess of stannous chloride, added drop by drop while agitating the solution. Wash sides of beaker with distilled water and cool rapidly. Add 10 cc. of mercuric chloride solution and stir vigorously for about thirty seconds.[4] Pour the mixture into a large porcelain casserole or dish containing 20 cc. of the manganese solution in about 500 cc. of water which has just been tinted with the permanganate solution.

[1] The contents of the funnel will remain hot if the solution in the beaker is kept hot over a low flame and filtration is fairly rapid.

[2] Heat over Bunsen to redness before placing over blast in order to prevent loss of precipitate by blowing out of crucible.

[3] Analyst, **34** (1909), 306.

[4] Barneby has shown that only a short interval of time is necessary between the addition of mercuric chloride and manganese sulphate, if the solution is thoroughly agitated. J. Am. Chem. Soc., **36** (1914).

te with N/40 permanganate solution, to original tint and correct result by the ne of $KMnO_4$ required for a blank containing the same quantity of HCl (diluted), ıg 2 or 3 drops of stannous chloride to the hot solution, cooling, adding 10 cc. ercuric chloride and titrating similarly.

'hen the rock solution contains carbonaceous matter it is necessary first to se this with a little potassium chlorate, evaporate to dryness to eliminate chlorine, edissolve with 5 cc. conc. HCl and about 10 cc. of water.

alculate the Fe_2O_3 found to $FePO_4$, using the factor 1.8898, and after deducting the weight of combined phosphates found, calculate the difference ($AlPO_4$) $_2O_3$.

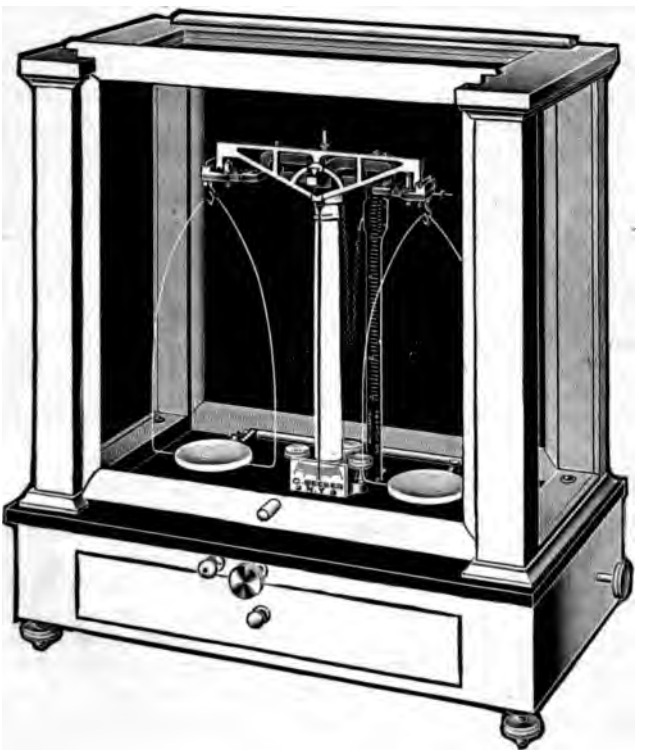


FIG. 55a.—Christian Becker Chainomatic Balance.

he chain balance shown in Fig. 55*a* is of the usual construction of the analytical or atory balances as far as knife edges, bearings, etc., are concerned, with the exception there is no rider and consequently no graduations on the beam. One end of veighing chain is hung from an arm of the scale beam, and the other end from le-block which is moved up and down on a vertical graduated scale. As this is raised, more of the weight of the chain is taken from the beam and hangs the slide-block which forms a stationary support for holding the inactive part e chain. As the slide is lowered a greater proportion of the weight of the chain nsferred to the beam. By means of this chain and vernier device, after all the sary large weights up to 50 milligrams are placed on the pan, the weighing from illigrams to $\frac{1}{10}$ of a milligram can be concluded without opening the balance or the arrest, eliminating the necessity of reading and replacing all small weights or ndling of a rider, with a consequent enormous saving of time. The editor has used ecker chainomatic balance for over a year and has found it highly satisfactory.

PLATINUM

R. E. HICKMAN[1]

Pt, *at.wt.* 195.2; *sp.gr.* 21.48; *m.p.* 1755° C.; *oxides* PtO, PtO_2

DETECTION

Platinum is a gray, lustrous, soft and malleable metal. It is not altered by ignition in the air, but fuses in the oxy-hydrogen flame. It does not dissolve in any of the single acids, but a fusion with acid potassium sulphate attacks the metal slowly. The action of chlorine in general, and nitro-hydrochloric acid (aqua regia), the main solvent, converts the metal to hydrochlorplatinic acid, H_2PtCl_6, which forms many double salts, or platinochlorides. If platinic chloride is gently heated it breaks up into platinous chloride, $PtCl_2$, and chlorine.

If, however, the platinum is alloyed with silver, it dissolves in nitric acid to a yellow liquid, provided sufficient silver is present in the alloy.

The oxides can be formed by carefully igniting the corresponding hydroxides. These are very unstable, decomposing into metal and oxygen by gentle ignition.

The chlorides are the most important compounds of platinum. Two complex acids are formed with hydrochloric acid when the metal is dissolved in aqua regia.

$PtCl_4 + 2HCl = H_2PtCl_6$ (hydrochlorplatinic acid), orange-red crystals.

$PtCl_2 + 2HCl = H_2PtCl_4$ (hydrochlorplatinous acid), only known in solution.

An aqueous solution of the former is yellowish-orange, while an aqueous solution of the latter is dark brown, the former being by far the more important.

Potassium iodide precipitates platinum iodide, but it dissolves quite readily, giving a pink to a dark blood-red liquid, depending on the concentration of the solution. Nitric acid should be absent. Heat destroys this color, as well as hydrogen sulphide, sodium thiosulphate and sulphite, sulphurous acid, mercuric chloride and certain other reagents.

Hydrogen sulphide precipitates black platinum disulphide, PtS_2, with the other elements of the hydrogen sulphide group. The solution should be warm, as precipitation takes place more quickly. It is difficultly soluble in ammonium sulphide. It will be found in the extract with the arsenic, antimony, tin, gold, molybdenum, etc., and is precipitated with these elements upon addition of hydrochloric acid. Platinum sulphide is soluble in aqua regia.

Ammonium chloride added to a concentrated solution of platinum chloride precipitates yellow $(NH_4)_2PtCl_6$, which is slightly soluble in water, but insoluble in dilute ammonium chloride solution and alcohol.

Potassium chloride precipitates yellow K_2PtCl_6, which is difficultly soluble in water, but insoluble in 75% alcohol.

[1] Chief Chemist, J. Bishop & Co. Platinum Works.

Ferrous sulphate precipitates metallic platinum on boiling from a neutral solution. Neutralize with Na_2CO_3. Free mineral acids prevent the precipitation (difference from gold).

Stannous chloride does not reduce platinum chloride to metal, but reduces hydrochlorplatinic acid to hydrochlorplatinous acid.

$$H_2PtCl_6+SnCl_2=H_2PtCl_4+SnCl_4.$$

Oxalic acid does not precipitate platinum (difference from gold).

Sodium hydroxide with glycerine reduces hydrochlorplatinic acid on warming to black metallic powder.

Formic acid precipitates from neutral boiling solutions all the platinum as a black metallic powder.

Thallium protoxide precipitates from the platinum bichloride solution a pale yellow salt, thallium platinochloride. When the salt is heated to redness it leaves an alloy of thallium and platinum.

Rubidium, caesium and thallium chlorides yield similar insoluble salts with platinum chloride.

Sodium hydroxide added to platinic chloride and then supersaturating with acetic acid produces a reddish-brown precipitate of platinic hydroxide $Pt(OH)_4$. This dissolves in acids readily, except acetic acid.

Metallic zinc, magnesium, iron, aluminum and copper are the most important metals that precipitate metallic platinum.

$$H_2PtCl_6+3Zn=3ZnCl_2+H_2+Pt.$$

ESTIMATION

Platinum may be present under the following conditions:

1. Native grains usually accompanied by the other so-called platinum metals, iridium, palladium, ruthenium, rhodium, osmium, and gold and silver (alloyed with one or more of the allied metals).

Ore concentrates containing the native grains as above with the base metals, iron, copper, chromium, titanium, etc. The associated minerals high in specific gravity in the gravels may be expected to appear with the platinum nuggets, such as chromite, magnetite, garnet, zircon, rutile, small diamonds, topaz, quartz, cassiterite, pyrite, epidote, and serpentine; with gold in syenite; ores of lead and silver.

2. Scrap platinum containing, oftentimes, palladium, iridium, gold, silver and iron.

3. Small amounts of platinum in the presence of large amounts of iron, silica, carbon, magnesia: platinum residues, nickel and platinum contacts, photography paper, jewelers' filings and trimmings, dental and jewelers' sweeps and asbestos, etc.

4. Platinum alloyed with silver, gold, tungsten, nickel, copper, lead, etc.

5. Platinum solutions and salts.

Preparation and Solution of the Sample

The best solvent for platinum is aqua regia. The metal is also acted upon by fusion with the fixed alkalies—sodium or potassium hydroxide and sodium peroxide or potassium or sodium nitrate; also by fusion with acid potassium sul-

phate. Platinum alloys when highly heated with other metals, as lead, tin, bismuth, antimony, silver, gold, copper, etc. The element dissolves in nitric acid when alloyed with silver. This gives a method for the determination of gold in the presence of silver and platinum alloy.

All salts of platinum are soluble in water. The less soluble salts are the chloroplatinates of potassium, ammonium, rubidium, and caesium. Heat increases the solubility while the presence of alcohol decreases the solubility.

Ores. When the free grains of platinum, gold and osmiridium are desired the following method is recommended: Five to 10 grams of the ore are taken from a well-mixed pulverized sample and placed in a large platinum dish that has been weighed. Twenty-five to 50 cc. of strong hydrofluoric acid together with 5 to 10 cc. of concentrated sulphuric acid is mixed with the ore in the dish and evaporated on the water bath, when SiF_4 and the excess of HF are expelled. The material is gently heated until SO_3 fumes are given off. This is repeated with HF if necessary. The material is washed into a casserole with about 200 cc. of hot water and digested over a water bath for fifteen or twenty minutes, and is then washed by decantation, several times pouring the supernatant liquor through a filter to save any floating material that might be washed out. The filter is cautiously burned and the residue is added to the unattacked material. This is transferred from the dish to a beaker or a porcelain dish and treated with aqua regia. The platinum and a small amount of iridium that dissolves with the platinum on account of its being alloyed can be precipitated with ammonium chloride. The remaining residue in the dish will be a small amount of sand and osmiridium. The silica is driven off with HF as described above and the bright grains weighed as osmiridium, or the sand and osmiridium are run down in a scorifier with lead, and the lead dissolved in dilute nitric acid, leaving the osmiridium grains free from sand.

Platinum Scrap. One-half gram to a gram is dissolved in aqua regia and evaporated with HCl to get rid of the HNO_3.

If the platinum is alloyed with a large amount of copper, silver, lead and other impurities, a sample of 1 to 5 grams is dissolved in 15 to 25 cc. of HNO_3, whereby the copper, silver, lead and other impurities alloyed with the platinum as well as a large amount of platinum will dissolve. The residue after washing will be platinum and gold. These are dissolved in aqua regia as described above and the platinum precipitated with ammonium chloride. The platinum is recovered from the nitric acid solution and added to the aqua regia solution and the whole is evaporated to get rid of the HNO_3.

Small Amounts of Platinum in the Presence of Large Amounts of Iron; Iron Scale, Fe_2O_3; Sulphate of Iron, Magnesia, Sulphate of Magnesia, Silica, etc. The material is carefully weighed and the coarse scales are separated from the finer material containing the platinum by passing the fines through a 20-in. mesh or finer wire sieve. The coarse scale seldom contains platinum, but it is advisable to quarter this down to 1 kilogram or a fairly good-sized sample and test for platinum on a portion of the ground sample. This can be tested by a wet or a fire assay. The fines are quartered down to about 1 kilogram and ground to pass a 60- to 80-in. mesh sieve. One hundred to 500 grams of the material are taken for analysis. This is placed in one or more casseroles, depending on the amount taken. Each 100-gram portion is extracted by digestion on the steam bath with about 300 to 400 cc. of 10% H_2SO_4. The iron, magnesia, etc., soluble in H_2SO_4 will go into solution, leaving the platinum with the

insoluble residue. Filter (a Büchner funnel may be necessary) and wash the residue with water. Test the filtrate for platinum and if any is present precipitate with zinc as described below.

After the filter is ignited in a large platinum dish, the residue is moistened with H_2SO_4, and HF is added completely covering the material. The solution is evaporated on the water bath until SO_3 fumes are given off. If necessary, repeat the treatment with H_2SO_4 and HF until all the silica is driven off as SiF_4. The residue is transferred to a casserole and digested with aqua regia according to directions given under Ores and Platinum Scrap. It is sometimes very difficult to precipitate all of the platinum in the presence of a large amount of iron, magnesia, etc., not having the solution concentrated enough for the platinum. It is advisable to reduce the platinum by iron or zinc, filter, wash with water and redissolve the black metallic platinum in aqua regia. The HNO_3 is expelled by evaporation and adding concentrated HCl from time to time and finally the platinum is precipitated with ammonium chloride.

SEPARATIONS

A careful review of the paragraph on Detection will be very helpful oftentimes in making separations from other metals and substances.

Separation of Platinum from Gold. The platinum is precipitated first with ammonium chloride, as $(NH_4)_2PtCl_6$. After the precipitate has settled it is filtered and washed free from gold with dilute ammonium chloride solution and alcohol. The gold is precipitated with a concentrated solution of ferrous sulphate or iron protochloride as metallic gold.

Oxalic acid precipitates the gold, leaving the platinum in solution. The oxalic acid is added and the solution boiled until the gold is entirely precipitated. Filter and wash the precipitate of metallic gold free from platinum. The filtrate is evaporated as far as possible without crystallizing, and the platinum is precipitated with ammonium chloride as $(NH_4)_2PtCl_6$, or it may be reduced with zinc and the black dissolved in aqua regia and treated as described above.

Separation of Platinum from Iridium. The platinum and the iridium are precipitated by iron or zinc and the black residue is washed free from impurities and the platinum is dissolved in dilute aqua regia with gentle heating, leaving the iridium as metallic iridium. The platinum solution is evaporated as described above and precipitated with NH_4Cl as $(NH_4)_2PtCl_6$.

If the platinum and iridium are precipitated together, the salt is filtered and washed with ammonium chloride solution and finally ignited. The sponge is redissolved and evaporated as above to expel the HNO_3. The platinum and the iridium are precipitated with NaOH, which brings down the platinum and iridium as $Pt(OH)_4$ and $Ir(OH)_4$. Boil this mixture with alcohol, which reduces the $Ir(OH)_4$ to $Ir(OH)_3$, but does not affect the $Pt(OH)_4$. Dissolve these hydroxides in HCl, forming $PtCl_4$ and $IrCl_3$ in solution, and the platinum is precipitated with NH_4Cl free from iridium.

Separation of Platinum from Palladium. The platinum and the palladium are reduced with zinc and the black residue treated with HNO_3. The palladium goes into solution, leaving the platinum as a black metallic residue.

The black residue of platinum and palladium can be dissolved in aqua regia and the solution evaporated with additions of HCl to get rid of the nitric acid.

The platinum is precipitated with NH_4Cl and filtered. The filter is washed free from palladium.

Separation of Platinum from Ruthenium. From the chloride of platinum and ruthenium the metals are precipitated with ammonium or potassium chloride and filtered. The filter is washed with dilute ammonium chloride solution or dilute potassium chloride solution and alcohol until free from ruthenium. If a large quantity is handled it may be necessary to ignite to platinum sponge and dissolve in aqua regia, expel the HNO_3 as described above, and reprecipitate with NH_4Cl, filter and wash free from ruthenium.

Separation of Platinum from Rhodium. The rhodium salt, like the ruthenium salt, is soluble and can be washed from the platinum salt, $(NH_4)_2PtCl_6$, as under Separation of Pt from Ru.

Separation of Platinum from Osmium. Both metals are reduced with zinc as a fine black powder. The metallic residue is washed and carefully ignited at a high temperature under a hood, as the fumes are poisonous and disagreeable like chlorine. The osmium will be converted into OsO_2 and OsO_4, which are very volatile. The residue is dissolved in aqua regia and the platinum is precipitated with NH_4Cl.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM

A. Weighing as Metallic Platinum

1. When the platinum contains only a small amount of impurities a sample of $\frac{1}{10}$ gram or more is taken and dissolved in aqua regia. The solution is gently heated until all is dissolved, adding another portion of aqua regia if necessary. The solution is evaporated, adding HCl from time to time in order to expel the HNO_3. Filter and evaporate again to concentrate the solution. Precipitate with ammonium chloride. After stirring, let stand until the precipitate, $(NH_4)_2PtCl_6$, settles, overnight if convenient. Filter, wash with alcohol or ammonium chloride solution and alcohol, and ignite to metal, which will be in the form of metallic sponge. Cool in a desiccator and weigh as metallic platinum.

$$\frac{\text{Wt. of Pt found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in the material.}$$

2. When the platinum solution contains a large amount of impurities, as iron, nickel, magnesia, etc., it is advisable to reduce the platinum to black metallic platinum with zinc, iron or magnesium as follows: The solution is made acid (2 to 5% free HCl) by adding HCl. The Zn, Fe or Mg is added in small quantities at a time until the solution becomes colorless or until the platinum is completely precipitated.[1] After action has ceased the platinum black metal is filtered onto an ashless filter paper and washed with warm dilute HCl to remove any excess Zn, Fe, or Mg that might be present. The filter and its contents are

[1] $FeCl_3$ in presence of HCl has a solvent action on platinum, hence the iron should be completely reduced.

carefully ignited and afterwards dissolved in aqua regia and treated as directed under A, 1.[1]

3. If none of the other Hydrogen Sulphide Group metals are present the platinum can be precipitated by hydrogen sulphide, filtered, washed with hot water and ignited to metal. If impurities are present in the sulphide, dissolve in aqua regia and proceed as under A, 1.

B. Weighing as a Salt

1. The procedure is the same as under A. The $(NH_4)_2PtCl_6$ precipitate is washed on a weighed Gooch crucible with alcohol. The crucible and contents are dried at a temperature below 100°. Cool in a desiccator and weigh as $(NH_4)_2PtCl_6$.

$$\text{Wt. of } (NH_4)_2PtCl_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } (NH_4)_2PtCl_6} \times \frac{100}{\text{Wt. of sample}} = \text{per cent of Pt in material.}^2$$

2. After proceeding as described under A, the platinum is precipitated with potassium chloride as K_2PtCl_6. Transfer to a weighed Gooch crucible and wash well with alcohol. Dry below 100°, cool in a desiccator and weigh as K_2PtCl_6.

$$\text{Wt. of } K_2PtCl_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } K_2PtCl_6} \times \frac{100}{\text{Wt. of sample}} = \% \text{ of Pt in material.}^3$$

C. Determination of Platinum by Electro-analysis

When platinum solutions are acidulated with sulphuric acid and acted upon by a feeble current they give up the metal as a bright deposit upon the electrode. If platinum is used as the electrode, first coat it with a layer of copper and deposit the platinum upon the copper. Wash with water and alcohol and after drying weigh.

$$\text{Wt. of electrode} + \text{Cu} + \text{Pt} - \text{Wt. of electrode} + \text{Cu} = \text{Wt. of Pt.}$$

$$\frac{\text{Wt. of Pt}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in material.}$$

Dr. E. F. Smith, in his work on "Electro-Analysis" recommends that the K_2PtCl_6 be dissolved in water and slightly acidulated with H_2SO_4 (2 or 3% by vol.) and after heating to about 60 to 65° and electrolyzing with $N.D._{100} = .05$ ampere and 1.2 volts, the platinum will be completely precipitated in from four to five hours in a perfectly adherent form. A rotating anode will precipitate the platinum much quicker.

[1] If iron and lead are suspected, the platinum residue is washed with 10% solution of ammonium chloride and then with 10% solution of ammonium acetate and finally with 80% alcohol.

[2] Factor $(NH_4)_2PtCl_6$ to Pt = 0.4393.

[3] Factor K_2PtCl_6 to Pt = 0.4013.

RARER ELEMENTS OF THE ALLIED PLATINUM METALS

E. E. Hoffman[1]

IRIDIUM

Element, Iridium. **Ir. *at.wt.* 193.1; *sp.gr.* 22.3; *m.p.* 2350° C.? *oxides* IrO_2, Ir_2O_3.**

DETECTION

Iridium is found associated with platinum. The element is insoluble in all acids, including aqua regia. Chlorine is the best reagent which forms the chlorides of iridium and yields compounds with other chlorides as K_2IrCl_6, which is insoluble. If the element is heated in a stream of chlorine in the presence of potassium chloride there forms a salt, K_2IrCl_6, which is sparingly soluble and is used in the separation of iridium.

Caustic Alkalies produce in a boiling solution a dark-blue precipitate of $Ir(OH)_4$ insoluble in all acids except HCl.

Potassium chloride forms the double salt of K_2IrCl_6, which is black and is difficultly soluble in water.

Ammonium chloride precipitates black $(NH_4)_2IrCl_6$, which is difficultly soluble in water.

Hydrogen sulphide precipitates black Ir_2S_3, soluble in $(NH_4)_2S$.

Metallic zinc precipitates from an acid solution black metallic iridium.

Formic acid and sulphurous acid precipitate black metallic iridium from hot solutions.

ESTIMATION

Substances in which iridium is determined are few, namely: platinum scrap, jewelers' sweeps, contact points, ores, etc.

Preparation and Solution of the Sample

Platinum scrap and contact points, etc., containing iridium dissolve with difficulty in aqua regia, depending on the amount of iridium present. The alloy is dissolved quicker if it is rolled or hammered to a very thin sheet or ribbon. The alloy of platinum and iridium with an iridium content up to 10% dissolves in aqua regia slowly; an alloy of iridium content of 15% dissolves in aqua regia very slowly and the aqua regia will likely have to be replenished from time to time. An alloy of 25% iridium is practically insoluble in aqua regia. The fillings from the sweeps, etc., can be dissolved by aqua regia the same as the scrap. After expelling the HNO_3 the platinum and the iridium are precipi-

[1] Chemist, J. Bishop & Co. Platinum Works.

tated together with NH_4Cl as $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. When the precipitate is ignited to metal it forms an alloy of platinum and iridium. The iridium imparts a pinkish to a scarlet color to the salt, depending on the amount of iridium present.

If the iridium content is high the metal can be mixed with NaCl, heated to a dull red heat in a porcelain or silica tube, and moist chlorine passed over the mixture. The iridium will be in the form of a chloride which dissolves in water. After filtering the solution and evaporating with HCl, the iridium as well as the platinum is precipitated with NH_4Cl or H_2S. This is a convenient way on a larger scale to dissolve osmiridium in ores. The writer has had good results with this operation.

When the iridium is contaminated with a large amount of impurities, it may be reduced from the solution with zinc, and the impurities dissolved by HNO_3 and dilute aqua regia; the residue is washed and dried as iridium.

Clean osmiridium grains are also brought into solution by a fusion of KNO_3, $NaNO_3$ or $KClO_3$ and NaOH or KOH, leaving the iridium as a bluish black oxide, Ir_2O_3.

Separations

Separation of Iridium from Platinum. See Separation of Pt from Ir.

If the platinum and iridium are alloyed with ten times their weight of silver and the alloy dissolved in HNO_3, the silver and the platinum dissolves, leaving the iridium insoluble. After washing the residue, treat with a small amount of dilute aqua regia to dissolve any platinum that may be present.

For other separations see Separations under Pt and the other metals.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRIDIUM

Iridium is nearly always weighed as the metal.

1. By Reduction with Zinc

The solution of iridium or iridium and platinum is treated with C.P. granulated zinc and 5% free HCl. The iridium and the platinum are precipitated as fine black metal. The black metal is washed free from impurities and the platinum is dissolved in dilute aqua regia as described under the Separations. The insoluble portion is dried and weighed as iridium.

2. By Igniting the Salt $(NH_4)_2IrCl_6$

When the iridium content is low and the platinum and the iridium are precipitated together with NH_4Cl, the iridium imparts a pinkish to a deep-red color to the salt, depending on the amount of iridium present. The percentage of iridium in the salt can be judged fairly well by comparing with standard iridio-platinum salts. The salt is filtered, washed with alcohol and carefully ignited and weighed as iridio-platinum sponge metal. The percentage of iridium in

the sample can be obtained from the weight of the iridium calculated from the percentage of iridium in the salt.

$$\frac{\text{Per cent of Ir found in the salt} \times \text{Wt. of iridio} - \text{Pt found}}{\text{Wt. of sample taken}} \times 100 = \% \text{ of Ir in material.}$$

When the iridium is in solution from the chlorine method, the solution is filtered and concentrated with HCl and the iridium precipitated with NH_4Cl. The salt $(NH_4)_2IrCl_6$ is filtered and washed with alcohol and carefully ignited to iridium sponge. Treat with a few drops of formic acid to reduce any oxide that may form or reduce with hydrogen and weigh as metallic iridium.

$$\frac{\text{Wt. of Ir found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Ir in material.}$$

3. By Obtaining it as a Residue

The iridium and the platinum, etc., are alloyed with ten times its weight of silver and the alloy dissolved in HNO_3. The residue will be a small amount of platinum, gold, if any present, and iridium. Add a small amount of dilute aqua regia, which will dissolve the gold and the rest of the platinum, leaving the iridium as a black residue. This is filtered, washed and ignited and weighed as metallic iridium.

PALLADIUM

Element, Palladium. **Pd. *at.wt.* 106.7; *sp.gr.* 11.9; *m.p.* 1549° C.; *oxides* Pd_2O, PdO, PdO_2.**

DETECTION

This metal is also found associated with platinum and iridium as well as ruthenium, rhodium, and osmium. It occurs in the metallic state sometimes with gold and silver. It resembles platinum as to luster and color. Palladium sponge when heated slightly gives a rainbow effect due to the formation of oxides. Hydrogen passed over the sponge restores it to the original color. It dissolves in HNO_3 and boiling H_2SO_4. HCl has little action upon it. It is readily soluble in aqua regia, forming $PdCl_2$.

Alkalies precipitate a dark-brown precipitate soluble in an excess of the reagent. If boiled a brown palladous hydroxide is precipitated. The anhydrous oxide is black.

Ammonia gives a flesh-red precipitate, $PdCl_2NH_3$, soluble in excess of ammonia. If HCl is added to this solution the yellow compound of pallad-ammonium chloride, $Pd(NH_3Cl)_2$, is deposited.

Mercuric cyanide precipitates a yellowish-white gelatinous precipitate, $Pd(CN)_2$, insoluble in dilute acids, but dissolving in ammonia and in potassium cyanide to $K_2Pd(CN)_4$.

Potassium iodide precipitates black palladous iodide, PdI_2, insoluble in water, alcohol, and ether, but soluble in an excess of the reagent.

Hydrogen sulphide precipitates black palladous sulphide, PdS, soluble in HCl and aqua regia, but insoluble in $(NH_4)_2S$.

Potassium nitrite precipitates a yellow crystalline powder, $K_2Pd(NO_2)_4$.

Ferrous sulphate slowly produces a black precipitate of metallic palladium from the nitrate.

Ammonium chloride precipitates palladium as $(NH_4)_2PdCl_4$ from the nitrate.

Formic acid, zinc and iron reduce to metallic palladium.

ESTIMATION

Palladium is determined in alloys, ores, jewelers' sweeps, etc.

Preparation and Solution of the Sample

The solubility of palladium has been taken up under Detection. Palladium when alloyed with platinum, or an alloy of platinum, iridium and palladium, dissolves with the other metals in aqua regia as the chloride. When palladium is alloyed with silver the palladium and silver are dissolved in HNO_3, from which the silver can be separated.

Separations

Separation of Palladium from Platinum and Iridium. The chlorides of palladium, platinum and iridium in solution must be free from HNO_3. The platinum and the iridium are precipitated with NH_4Cl, leaving the palladium in solution. The precipitate is put on a filter and washed free from Pd with NH_4Cl solution and alcohol.

Separation of Palladium from Silver and Gold. Three times the weight of the gold in silver should be present in the alloy in order to separate the silver and palladium from the gold. The silver and the palladium will dissolve in HNO_3, leaving the gold as the residue. This is filtered off and the silver may be precipitated with HCl. The silver chloride is filtered off and washed with hot water until free from Pd.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM

1. The palladium is precipitated from the solution by granulated zinc, the solution having a small amount of free hydrochloric acid. The residue, after the zinc is dissolved, is put on a filter and washed free from impurities. Ignite the filter and dissolve in a small amount of aqua regia and evaporate with additions of HNO_3 to get rid of the HCl. Dilute with a small amount of water and precipitate the palladium with NH_4Cl crystals. Heat for a few minutes and let cool. Filter, wash with alcohol, and ignite. Moisten with formic acid to reduce to metal any oxide that may have formed. Dry and weigh as metallic palladium.

$$\frac{\text{Wt. of Pd found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pd in material.}$$

2. With the solution containing about one-fifth the volume of free HCl, the palladium is precipitated with 10% KI solution. Heat to nearly boiling, filter, wash free from iron, etc., with 1 : 4 HCl. Ignite, cool, moisten with formic acid, dry and weigh as metallic Pd.

3. The filtrate from the platinum precipitation or the solution containing the Pd is made to about 150 cc., and the Pd is precipitated by adding a solution of dimethylglyoxime (1 gram in 5 cc. HCl). Bring to boiling and let stand overnight if convenient. Filter on a weighed Gooch crucible and wash with water acidified with HCl, then with alcohol. Dry and weigh as $(C_8H_{14}N_4O_4)_2Pd$, which contains 31.68% Pd.

4. The nitric acid in the palladium solution is expelled by evaporating with HCl. Neutralize the chloride solution almost completely with sodium carbonate and mix the solution with a solution of mercuric cyanide, $Hg(CN)_2$, and heat gently for some time. Let stand until cool, overnight if convenient. A yellowish-white precipitate of $Pd(CN)_2$ is formed. Filter, wash with 1% $Hg(CN)_2$ solution, ignite and reduce in hydrogen to metal, or reduce with formic acid, dry, and weigh as metallic Pd.

RUTHENIUM

Element, Ruthenium. **Ru.** ***at.wt.*** **101.7;** ***sp.gr.*** **12;** ***.pm.*** **2450° C.?** ***oxides*** **RuO, Ru_2O_3, RuO_2, RuO_4.**

DETECTION

This element is found only in platinum ores. It is barely soluble in aqua regia, and insoluble in acid potassium sulphate. It dissolves when fused with KOH and KNO_3. The solution of the fusion when dissolved in water forms potassium rutheniate, K_2RuO_4, from which HNO_3 precipitates the hydroxide, which is soluble in HCl. The treatment with chlorine and KCl at a high temperature yields a salt of K_2RuCl_6. The salts that are most common are K_2RuCl_5 and K_2RuCl_6.

Potassium hydroxide precipitates a black hydroxide easily soluble in HCl.

Hydrogen sulphide slowly produces black Ru_2S_3.

Ammonium sulphide precipitates brownish black sulphide.

Metallic zinc precipitates metallic ruthenium, the solution first turning blue.

ESTIMATION

Ruthenium is generally estimated in alloys and ores or residues.

Preparation and Solution of the Sample

When ruthenium is alloyed with platinum or gold, aqua regia dissolves these metals, forming the chlorides of platinum, gold and ruthenium. The ruthenium in ores is in the form of an alloy with platinum or osmiridium. This is fused with KNO_3 and KOH in a silver crucible, the osmium and the ruthenium forming salts as described above, while the iridium remains as an oxide.

Separations

Separation of Ruthenium from Platinum. The two metals are precipitated with KCl and the potassium rutheniochloride is dissolved out with cold water containing a very small amount of KCl and alcohol. The ruthenium is then precipitated from an acid solution by additions of granulated zinc.

A separation may be made by alloying with silver and dissolving the platinum and silver by HNO_3, the ruthenium remaining as the residue.

Separation of Ruthenium from Iridium. The two metals are fused with KOH and KNO_3 as described above, the ruthenium forming a salt soluble in water and the iridium remaining as an oxide.

To the solution of the two metals, sodium nitrite is added in excess, with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is boiled until an orange color appears. The ruthenium and the iridium are converted into soluble double nitrites. Sodium sulphide is then added, small quantities at a time until the precipitated ruthenium sulphide is dissolved in the excess of alkaline sulphide. At first the addition of the sulphide gives the characteristic crimson tint due to ruthenium, but this quickly disappears and gives a bright chocolate-colored precipitate. The solution is boiled for a few minutes, and allowed to become perfectly cold and then dilute HCl cautiously added until the dissolved ruthenium sulphide is precipitated and the solution is faintly acid. The solution is filtered and the precipitate washed with hot water. The filtrate will be free from ruthenium.[1]

Separation of Ruthenium from Rhodium. The mixed solution of the two metals is treated with potassium nitrite as described above. The orange-yellow solution is evaporated to dryness upon the water bath and treated with absolute alcohol. The rhodium remains undissolved and can be filtered off and washed with alcohol. The rhodium salt can be ignited with NH_4Cl and after washing yields metallic rhodium.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF RUTHENIUM

Ruthenium is best weighed as the residue after the other metals are eliminated. It may be precipitated from the solution with zinc and after filtering, washing and igniting the filter the impurities are dissolved in aqua regia. The residue is ruthenium. The metals may be alloyed with silver and after dissolving out the silver, platinum and palladium with HNO_3, the residue is treated with aqua regia, leaving the residue as ruthenium. If iridium is present in the residue, weigh as iridium and ruthenium. Make a fusion with KOH and KNO_3 as described under iridium and filter off the Ir_2O_3. Calculate the weight of Ir which is to be subtracted from the weight of the ruthenium and iridium. The difference is ruthenium.

The solution of Ru_2Cl_6 is evaporated to drive off the excess acid and then taken up with 50 to 60 cc. of water and a few pieces of magnesium added gradually. The solution is filtered and the residue washed with a 5% H_2SO_4 solution to get rid of any magnesium that may be present. Ignite at the lowest possible temperature, and heat in hydrogen to red heat, cool and weigh as metallic ruthenium.

[1] "Select Methods in Chemical Analysis," Sir. Wm. Crookes.

RHODIUM

Element, Rhodium. **Rh, *at.wt.* 102.9; *sp.gr.* 12.1; *m.p.* 1950° C.; *oxides* RhO, Rh_2O_3, RhO_2.**

DETECTION

Rhodium is found only in platinum ores. It is a white metal, difficultly fusible, and insoluble in acids. Rhodium, however, dissolves in aqua regia when alloyed with platinum, to a cherry red solution. It is also soluble in molten phosphoric acid and dissolves when fused with acid potassium sulphate with the formation of $K_3Rh(SO_4)_3$. If the metal is treated with chlorine in the presence of sodium chloride there forms a soluble salt, Na_3RhCl_6.

Hydrogen sulphide precipitates from a hot solution and incompletely a brown rhodium sulphide, Rh_2S_3.

Potassium hydroxide precipitates at first a yellow hydroxide, $Rh(OH)_3+H_2O$ soluble in an excess of the reagent. If boiled, a gelatinous, dark-brown hydroxide, $Rh(OH)_3$, separates. A solution of Na_3RhCl_6 does not show this reaction immediately, but the precipitate appears in the course of time. An addition of alcohol causes a black hydroxide to be precipitated at once.

Ammonium hydroxide produces a yellow precipitate of $Rh(NH_3)_3Cl_3$ which is insoluble in HCl.

Potassium nitrite precipitates from hot solutions a bright yellow precipitate of double nitrite of potassium and rhodium.

Zinc, iron and formic acid precipitate rhodium as a black metal.

Hydrogen reduces rhodium salts.

ESTIMATION

Rhodium is estimated mainly in ores, thermo couples and salts.

Preparation and Solution of the Sample

When rhodium is estimated in thermo couples or other alloys of platinum and rhodium the wire or sample is rolled to a thin ribbon and dissolved in aqua regia. Both metals will go into solution, forming the chlorides of rhodium and platinum. The aqua regia will have to be replaced from time to time, as the alloy dissolves slowly.

The rhodium from salts is precipitated with zinc and the black metallic rhodium cleaned with dilute aqua regia, filtered, washed, ignited and reduced with hydrogen.

Some alloys and ores are alloyed with silver and the silver and platinum are dissolved in HNO_3. The residue is cleaned with aqua regia, dried, and weighed as metallic rhodium. If the residue is ignited reduce with hydrogen.

Separations

Separation of Rhodium from Platinum. The alloys of platinum and rhodium (10%) dissolve slowly in aqua regia as stated above. After expelling the HNO_3 the metals are precipitated with NH_4Cl. The precipitate is filtered

and washed with dilute ammonium chloride solution, which dissolves the rhodium salt. A very small amount of rhodium will color the filtrate pink to a rose-red color, depending on the amount of rhodium present.

Separation of Rhodium from Iridium. See Separation of Rh from Pt.

A separation can be made by adding sodium nitrite in excess to the solution of the two metals, with a sufficient quantity of sodium carbonate to make the solution neutral or alkaline; this is boiled until the solution assumes a clear orange color. The rhodium and iridium are converted into soluble double nitrites. A solution of sodium sulphide is added in slight excess and the liquid made slightly acid. The rhodium is precipitated as dark-brown rhodium sulphide.

Separation of Rhodium from Ruthenium. The solution containing the two metals is treated with sodium nitrite as above and evaporated to dryness. The residue is powdered and treated in a flask with absolute alcohol. After filtering and washing with alcohol the rhodium remains undissolved.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF RHODIUM

From the solution of platinum and rhodium, the platinum is precipitated with NH_4Cl and the precipitate filtered off and washed free from rhodium with dilute ammonium chloride solution. The rhodium is precipitated with zinc and the residue is washed well with hot water acidulated with HCl. The residue is then cleaned with dilute aqua regia and the black metallic rhodium is filtered off, dried, and weighed as metallic rhodium. If the filter is ignited reduce in hydrogen before weighing.

The alloy may be melted with lead or silver and the buttons dissolved in HNO_3, leaving a residue which is treated with aqua regia to dissolve any platinum that might remain. Wash and weigh as metallic rhodium. If iridium is with the rhodium the residue is treated with salt and chlorine and the melt dissolved in water as described under Iridium. The iridium is precipitated with NH_4Cl and the rhodium with zinc. The rhodium black is cleaned with dilute aqua regia, filtered, washed and ignited. Reduce in hydrogen and weigh as metallic rhodium.

OSMIUM

Element, Osmium. **Os, *at.wt.* 190.9; *sp.gr.* 22.4; *m.p.* 2700° *C.? oxides* OsO, Os_2O_3, OsO_2, OsO_4.**

DETECTION

Osmium occurs with platinum ores and alloyed with iridium. The chlorides, $OsCl_3$ and $OsCl_4$, combine with the alkali chlorides. Osmium oxidizes easily and burns in the flame. Through the action of HNO_3, aqua regia or heating in a stream of moist chlorine, osmic tetroxide is formed. Osmium is very volatile and the fumes are poisonous. It is detected readily by the odor when heated, as the fumes are highly corrosive and disagreeable like chlorine. Chlorine passed over hot osmium mixed with KCl gives K_2OsCl_6, which dissolves in cold water.

Hydrogen sulphide precipitates brownish black osmium sulphide, OsS_4, but only in the presence of some strong mineral acid. It is insoluble in ammonium sulphide.

Potassium hydroxide precipitates reddish-brown osmium hydroxide.

Ammonium hydroxide precipitates the osmium hydroxide.

Zinc and formic acid precipitate black metallic osmium.

Hydrogen reduces osmium compounds to the metal.

ESTIMATION

Osmium is estimated mainly in osmiridium and platinum residues.

Preparation and Solution of the Sample

After the platinum is extracted the residue or osmiridium is mixed with two or three times its weight of common table salt. The mixture is put in a porcelain or silica tube and heated to a dull red heat; moist chlorine is then passed through the tube for a short time. The mass is cooled and dissolved with water. After several treatments the entire group of platinum metals will be in solution.

The osmium material may also be fused with KOH and KNO_3 and the melt dissolved in water. The osmium will be in solution as potassium osmate, K_2OsO_4, while the iridium remains as residue.

For Separations see below.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF OSMIUM

The osmium is very difficult to ascertain on account of the element being very volatile.

The potassium osmate, K_2OsO_4, solution is put in a small retort, and boiled with HNO_3, the vapor is conducted into NaOH solution and after acidifying with a little HCl the osmium can be precipitated with $Na_2S_2O_3$ as a brown precipitate of OsO_4 which is filtered, washed, dried and weighed as the oxide.

When osmuim is in the form of osmate of sodium the solution is heated gently and strips of aluminum are plunged in and the osmium will be deposited in metallic form, while the aluminum dissolves in the soda. Care must be taken not to add too much aluminum, as an aluminate might be precipitated which is troublesome. When the solution is discolored the dense precipitated osmium is washed by decantation with water to remove the sodium aluminate, and then with 5% H_2SO_4 solution to remove the excess aluminum. The osmium is dried in a bell-jar filled with hydrogen, then heated to a dull redness and cooled in a current of hydrogen. The osmium is weighed as the metal. As a check the osmium may be driven off in the form of OsO_4 by heating to redness with plenty of air, or better, in a current of oxygen and weighing again.[1]

[1] "Select Methods in Chemical Analysis," Sir Wm. Crookes.

ANALYSIS OF PLATINUM ORES

Take 3 to 5 grams of the ore and treat with aqua regia. After diluting, the osmiridium and gangue are filtered out, ignited and weighed. The insoluble portion is then fused in an assay crucible with at least twice the weight of granulated silver and borax glass. Clean the button and treat with dilute HNO_3, filter, wash free from silver, ignite and weigh as osmiridium.

The aqua regia solution is evaporated several times with HCl nearly to dryness. Then pass in a current of chlorine for thirty minutes, cool in chlorine and evaporate at 40° to a thick paste. Dilute with water, getting a clear solution of $PtCl_4$, $IrCl_4$, $RhCl_3$, $AuCl_3$, $PdCl_4$, $CuCl_2$ and $FeCl_3$. Saturate the solution with NH_4Cl and after forty-eight hours filter off the $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$; ignite in a porcelain crucible, adding crystals of ash-free oxalic acid toward the end. Digest the platinum and iridium sponge with 10% HCl, filter, ignite, reduce in hydrogen, cool in CO_2 and weigh as platinum and iridium (Ru). In the filtrate from the platinum and iridium, separate the palladium with dimethylglyoxime. Evaporate the filtrate to dryness and destroy the NH_4Cl by adding concentrated HNO_3 followed by concentrated HCl. Dissolve the residue in water and add $(NH_4)_2C_2O_4$ and heat from four to six hours till the gold is reduced; add dilute H_2SO_4, filter and wash with dilute H_2SO_4, then with dilute HCl, ignite and weigh as gold. Neutralize the excess acid with NH_4OH and precipitate any palladium in a boiling acid solution with dimethylglyoxime.

Treat the filtrate from the gold and palladium with 50 grams of pure zinc and 50 cc. of concentrated HCl; after five or six hours the solution should be colorless, otherwise add more HCl. Filter by suction and wash with dilute HCl, then with water till free from acid, dry the filter and ignite two or three hours; grind this in a glass mortar and digest two hours with HNO_3 (1 : 1), filter and wash with water; the residue is rhodium with traces of platinum and iridium. Evaporate the filtrate to dryness repeatedly with HCl and determine the copper.

Evaporate the filtrate from the copper to dryness, treating with HNO_3, then HCl; add water, HCl and zinc as above; add the ash to the main rhodium portion and grind in a glass mortar with acid potassium sulphate, $KHSO_4$, and fuse in a crucible; the rhodium is converted into a soluble sulphate, the iridium is oxidized and the platinum remains unaltered. Digest the melt with water and dilute HCl; a metallic residue is platinum or iridium. Filter and wash with very dilute HCl; to the filtrate add zinc to precipitate the rhodium, filter and wash with 5% H_2SO_4 solution, ignite and let cool. Finally ignite in hydrogen, cool in CO_2 and weigh. The insoluble residue from the $KHSO_4$ fusion is ignited, reduced and weighed. The platinum and iridium may be separated as described before.

Make up the filtrate from the first zinc reduction to 1 liter and treat 500 cc. with HNO_3 or H_2O_2; make two basic acetate precipitations and finally precipitate at 70° with NH_4OH, ignite and weigh as Fe_2O_3.

Calculation.

$$100 - \text{per cent sand} = A.$$

$$\frac{100}{A} = \text{factor by which per cent found is to be multiplied.}$$

[1] A modification of the Deville-Debray Procedure, by Wünder and Thuringer.

ASSAY METHODS OF PLATINUM ORES, ETC.

Take from 10 to 30 grams of the material and place in a 2½- or 3-in. scorifier with about 20 to 30 grams of test lead and cover with litharge. Fuse in a muffle for a half hour. When cool clean the lead button thoroughly and dissolve the lead with dilute nitric acid (1 : 3). When the lead is dissolved, filter, and wash the residue with hot water till free from lead. Dry the filter and remove the residue to a small glass beaker and burn the filter, after which the ash is added to the residue in the small glass beaker. This is treated with dilute aqua regia to remove any gold, platinum, etc., that may be present. Filter and wash thoroughly with hot water and ignite at a low temperature for a short time only, as osmium will volatilize. Weigh as osmiridium.

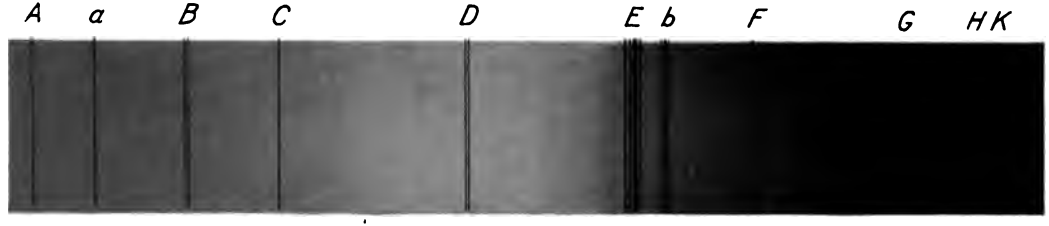
Take another portion of 10 to 30 grams of the material and treat with aqua regia two or three times. This will bring the platinum and the alloys (except osmiridium) into solution. After filtering make up the volume to 500 to 1000 cc., depending on the amount of platinum present. Take two or three portions of 25 to 50 cc. of the solution and evaporate to nearly dryness with additions of HCl to get rid of the HNO_3. Take up with a small amount of water and add ammonium chloride. Digest on the water bath and let cool overnight if convenient. Filter onto an ashless filter and wash with dilute ammonium chloride solution and alcohol. Ignite cautiously and weigh as platinum. The iridium will be precipitated with the platinum and weighed with the platinum; the color of the pure platinum precipitate is yellow, but the iridium precipitate will impart a pink to a deep red color to the platinum precipitate, and the per cent of iridium present can easily be judged by comparing with standard iridio-platinum salts.

The filtrate from the platinum precipitation is treated with ferrous sulphate to precipitate the gold. Digest and filter out the gold. Ignite and alloy with silver and part for gold.

To the filtrate from the gold add an excess of HCl and precipitate the palladium with 10% solution of potassium iodide as described under palladium. The palladium can be taken out before the gold by evaporating the filtrate from the platinum precipitation and precipitating the palladium with nitric acid and ammonium chloride as described under palladium.

In the filtrate from the palladium precipitation the rhodium is precipitated with zinc until the solution is colorless. Wash well with hot water and clean with dilute aqua regia. If this is done carefully the residue will be clean rhodium with probably a trace of iridium. Ignite the residue and reduce in hydrogen and weigh as rhodium.

If ruthenium and the total iridium content are to be estimated the separations are the same as described under these elements.



Diffraction Grating Spectrum

Prismatic Spectrum

PLATE III

POTASSIUM, SODIUM AND OTHER ALKALIES

W. B. Hicks.[1]

Sodium, Na, *at.wt.* 23.00; *sp.gr.* 0.9735; *m.p.* 97.6°; *b.p.* 877.5° C.; *oxides* Na_2O, Na_2O_2.

Potassium, K, *at.wt.* 39.10; *sp.gr.* 0.875; *m.p.* 62.5°; *b.p.* 757.5° C.; *oxides* K_2O, K_2O_4.

Lithium, Li, *at.wt.* 6.94; *sp.gr.* 0.534; *m.p.* 186°; *b.p.* >1400° C.; *oxide* Li_2O.

Rubidium, Rb, *at.wt.* 85.45; *sp.gr.* 1.532; *m.p.* 38.5°; *b.p.* 696° C.; *oxides* Rb_2O, Rb_2O_2, Rb_2O_3, Rb_2O_4.

Caesium, Cs, *at.wt.* 132.81; *sp.gr.* 1.87; *m.p.* 26.37°; *b.p.* 670° C.; *oxides* Cs_2O, Cs_2O_2, Cs_2O_3, Cs_2O_4.

DETECTION

Detection of Sodium

Sodium is usually identified by the color which it imparts to the flame or by means of the spectroscope. The solution is prepared as directed under Preparation and Solution of Sample, and is freed from all constituents other than the chlorides of magnesium and the alkalies according to the methods given under Separations. With exceedingly small amounts of sodium, it may be necessary to remove the magnesium also. After acidifying with hydrochloric acid, a drop of the solution is brought into the flame by means of a loop of platinum wire. In the presence of sodium, the flame assumes an intense yellow color, which is usually sufficient to identify the element. The results may be confirmed by examining the flame in the spectroscope, when the characteristic yellow sodium line will be prominent even in the presence of traces of sodium. As a matter of fact, the ever-presence of the sodium line is a hindrance to the success of the method, but by observing the sudden change in the intensity of the line, little trouble will be experienced in detecting exceedingly small amounts of the metal.

Sodium may also be detected by precipitation as sodium pyroantimonate, $H_2Na_2Sb_2O_7 \cdot H_2O$, from a sufficiently concentrated neutral or weakly alkaline solution by means of a solution of acid potassium pyroantimonate. The precipitate comes down in granular or crystalline form, and its formation is hastened by rubbing the sides of the vessel with a glass rod. In making this test, magnesium must also be previously removed from the solution.

In waters and soluble salts, it is usually sufficient to test directly the concentrated solution in the flame or spectroscope.

Detection of Potassium

For the detection of potassium in insoluble compounds, bring the sample into solution by one of the methods given under Preparation and Solution of

[1] Assistant Chemist, U. S. Geological Survey, Washington, D. C.

Sample. In other cases, prepare a strong solution of the material to be tested. Where only very small amounts of potassium are present, remove all the constituents from the solution except the chlorides of magnesium and the alkalies as directed under Separations. In the presence of considerable amounts of potassium, small quantities of other constituents will not materially interfere with the flame and spectroscopic tests. After acidifying with hydrochloric acid, bring a drop of the solution to be tested into the non-luminous flame and observe the color produced through a Merwin color screen.[1] In the presence of potassium, a distinct reddish-violet coloration will be apparent. This must not be confused with the color caused by large amounts of sodium, which appears bluish-violet through the screen. Comparison with the coloration produced by pure salts is advisable. If necessary, confirm the results by examining the flame in the spectroscope. In the presence of a moderate amount of a volatile potassium compound, a bright red line will be readily seen in the red portion of the spectrum, and a less distinct violet line will be visible far out in the violet rays.

Potassium may also be identified by various reactions, such as precipitation from a strong solution, as potassium chloroplatinate, perchlorate, acid tartrate, picrate, cobaltic nitrite, silico-fluoride, phosphotungstate, etc. These compounds of potassium are all sparingly soluble in water while the corresponding sodium salts are readily soluble.

Detection of Lithium

Bring the sample into solution as directed under Preparation and Solution of Sample, and separate the alkali chlorides from other constituents according to the methods under Separations. Digest the dry chlorides with amyl alcohol or with a mixture of absolute alcohol and ether, filter, and evaporate the filtrate to dryness. Moisten the residue with dilute hydrochloric acid and examine it in the spectroscope. A bright red band and a faint orange line make up the flame spectrum of lithium. These lie between the sodium line and the red potassium line and are easily recognized.

Lithium salts impart a carmine-red color to the flame, which is obscured by sodium, and by large amounts of potassium. But by the proper use of a color screen, the lithium flame may be recognized in the presence of large amounts of sodium.

Confirmation of the presence of lithium may be had by the formation of the sparingly soluble lithium phosphate or lithium fluoride.

Detection of Rubidium and Caesium

In the usual course of analysis, these rare elements are separated along with sodium, potassium, and lithium from all other bases. In order to detect rubidium and caesium, extract the dry chlorides of the alkali metals with a few drops of hydrochloric acid and 90% alcohol. This will dissolve most of the rare alkalies along with some sodium and potassium. Evaporate the solution to dryness, dissolve in a very small amount of water, and add chloroplatinic acid solution. Rubidium, caesium, and potassium chloroplatinates will be precipitated. Filter

[1] The Merwin color screens are manufactured and sold by G. M. Flint, 84 Wendell Street, Cambridge, Mass., at 25 cents apiece, and are far superior to the ordinary cobalt glass.

and wash the residue repeatedly with hot water to remove the potassium salt, which is much more soluble than rubidium and caesium chloroplatinates. During this treatment, examine the residue from time to time in the spectroscope. As the rubidium and caesium salts are concentrated through washing, their spectra will gradually become visible.

ESTIMATION

The estimation of sodium and potassium is required in the analysis of rocks, clays, soils, ashes of plants, waters, brines, saline deposits, salts of the alkalies, many technical products, and in other cases. The determination of potassium is of special importance in the analysis of fertilizers. The estimation of lithium is desired in the analysis of lithium minerals, frequently in mineral waters, occasionally in rocks, and in certain other special cases. The estimation of rubidium and caesium is seldom required.

Preparation and Solution of Sample

Procedure for Rocks and Other Insoluble Mineral Products. For silicate rocks and other silicious material, bring the alkalies into solution, according to the J. Lawrence Smith or the hydrofluoric acid method, as directed on pages 355 and 356. In the case of alunite prepare the solution as directed on page 356. For products which are dissolved by hydrochloric acid, effect the solution by acid digestion, expel the excess of acid by evaporation, and remove other constituents as directed under Separations.

Procedure for Soils.[1] Digest 10 grams of moisture-free soil with 100 cc. of hydrochloric acid of a constant boiling-point (sp.gr. 1.115) in a 300-cc. Erlenmeyer flask fitted with a ground-glass or rubber stopper and a reflux condenser. Digest continuously for ten hours on the steam bath, shaking the flask every hour. After settling, decant the solution into a porcelain dish. Wash the insoluble residue onto a filter with hot water, and continue the washing until free from chlorides, adding the washings to the original solution for evaporation. Oxidize the organic matter present in the solution with a few drops of nitric acid and evaporate to dryness on a water bath. Moisten with hydrochloric acid and dissolve in hot water and evaporate a second time to complete dryness and until the excess of hydrochloric acid is completely removed. Moisten the cooled residue with strong hydrochloric acid and dissolve in hot water. Filter into a 250-cc. graduated flask, wash free from chlorides, and dilute to the mark. Use an aliquot of 100 cc. for the determination of the alkalies.

Procedure for Fertilizers.[2] *Potash salts.* Boil 10 grams of the sample with 300 cc. of water for thirty minutes, wash into a 500-cc. graduated flask, cool, dilute to the mark, mix and pass through a dry filter. Determine the potassium in a 25-cc. aliquot representing 0.5 gram of the original substance, according to either the modified chloroplatinate or the Lindo-Gladding method.

Mixed fertilizers. Boil 10 grams of the sample with 300 cc. of water for thirty minutes, and wash into a 500-cc. graduated flask. Add to the hot solution a slight excess of ammonia and sufficient ammonium oxalate to precipitate all the lime, cool, dilute to the mark, mix, and pass through a dry filter. Evaporate

[1] U. S. Dept. Agr., Bu. of Chem., Bull. 107 (revised), 14, 1907.
[2] U. S. Dept. Agri., Bu. Chem. Bull. 107 (revised), 11, 1907.

50 cc. of the filtrate to dryness and ignite gently to remove ammonium salts. Dissolve in water, filter, and determine the potassium according to the modified chlorplatinate [1] or the Lindo-Gladding method.

Organic compounds. When it is desired to determine the total potash in organic substances such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly to loosen the mass from the dish, dissolve in water, filter, and determine the potassium according to the modified chloroplatinate or the Lindo-Gladding method.

If for any reason it is desired to use either the chloroplatinate or the perchlorate method in the determination of potassium, interfering substances, including sulphates, must first be removed from the solution.

Procedure for Ashes of Plants. Boil 20 grams of the sample with 300 cc. of water for thirty minutes, filter into a 500-cc. flask, and wash the residue thoroughly with hot water. Cool, dilute to the mark and mix. Take aliquots for the determination of the alkalies. The solution may also be prepared by digestion with hydrochloric acid.[2] This treatment is preferable when all the constituents of the ash are to be determined.

Procedure for Saline Residues, Soluble Salts, Brines, etc. In the case of water-soluble products, the convenience of the analyst usually determines the manner of preparing the solution. Usually it is preferable to weigh out a convenient portion, to make up the solution to definite volume, and to take an aliquot for each determination. As a general rule, a sample should be taken sufficient to give about a half gram of solids. Strong brines should be weighed and not measured.

SEPARATIONS

Separation of the Alkali Metals from other Constituents

Separation from the Hydrogen Sulphide and Ammonium Sulphide Groups of Metals

The alkali metals are usually weighed as chlorides or sulphates, and in general before undertaking their determination, all other bases and acids must first be separated from them. The hydrogen sulphide and the ammonium sulphide groups of metals are seldom to be found in solutions in which the determination of the alkalies is desired. If these are present, however, they may be readily precipitated by means of hydrogen sulphide and ammonium sulphide as detailed on pages 142 and 254.

Separation from Silica

Acidify the solution with hydrochloric acid and evaporate it in a platinum or porcelain dish on the water bath until the odor of hydrochloric acid in the dry residue can no longer be detected. Break up the dry mass with a platinum or glass rod, cool, moisten with a minimum amount of concentrated hydrochloric

[1] If this method is used, it will not be absolutely necessary to remove the calcium by addition of ammonia and amonium oxalate.

[2] Lunge, "Technical Methods of Analysis," 2, 456, 1911. D. Van Nostrand Co., New York.

acid, dissolve in a small quantity of water, filter and wash the residue free from chlorides. In the presence of much silica, repeat the operation.

Separation from Iron, Aluminum, Chromium, Titanium, Uranium, Phosphoric Acid, etc.

If phosphoric acid is present in amounts insufficient to combine with all the iron, alumina, etc., or is absent altogether, heat the solution to boiling, add a few drops of nitric acid to oxidize the iron, add gradually an excess of ammonia, boil for a minute or so, allow the precipitate to settle, and filter. Wash the precipitate free from chlorides with hot water.

If phosphoric acid is present in the solution in excess of that required to combine with the iron, alumina, etc., heat the solution to boiling, oxidize with nitric acid, add a slight excess of ferric chloride solution, and precipitate with ammonia as described above.

When the precipitate is considerable, it should be dissolved in hydrochloric acid, and the precipitation repeated.

If chromates are present, these must first be reduced to the chromic salt. For this purpose, add 10 to 15 cc. of hydrochloric acid and a small amount of alcohol to the solution and heat on the water bath or hot plate for a few minutes. Heat to boiling and precipitate with ammonia as directed above. The reduction may also be done by boiling with sulphurous acid.

Separation from Sulphates

Precipitate the sulphate radical as $BaSO_4$ by the addition of a slight excess of barium chloride to the hot solution as directed on page 395 for the determination of SO_4. Remove the excess of barium chloride by addition of ammonia and ammonium carbonate.

The two operations may be combined as follows: Add a slight excess of barium chloride to the hot solution and boil for a few minutes. Then, without filtering off the $BaSO_4$, add an excess of ammonia and ammonium carbonate, allow the precipitate to settle, filter, and wash free from chlorides.

Separation from Barium, Calcium and Strontium

To the not too concentrated solution, add a slight excess of ammonia and ammonium carbonate, heat to boiling, allow the precipitate to settle, filter and wash the residue a few times with hot water. Dissolve the precipitate, which is likely to contain small amounts of the alkalies, in a little dilute hydrochloric acid, and repeat the precipitation with ammonia and ammonium carbonate. Filter and wash the residue. Evaporate the combined filtrates to dryness in a platinum or porcelain dish and ignite cautiously at a very faint red heat to remove ammonium salts. Dissolve the residue in a little water, add a few drops of ammonia, ammonium carbonate, and ammonium oxalate, and allow to stand for several hours in order to precipitate the last traces of the alkaline earths. Filter and wash the residue free from chlorides.

Separation from Iron, Aluminum, Chrominum, Barium, Calcium, Strontium, Phosphates, Sulphates, etc., in One Operation

To the hot solution add a slight excess of barium chloride and boil for a few minutes. Then, without filtering off the $BaSO_4$, add an excess of ammonia and ammonium carbonate, heat to boiling, and allow the precipitate to settle. Filter and wash free from chlorides with hot water. After evaporating the filtrate to dryness, removing the ammonium salts by ignition, and dissolving the residue in a little water, precipitate the last traces of barium and calcium by addition of a few drops of ammonia, ammonium carbonate, and ammonium oxalate. By this procedure a small portion of the alkalies is retained by the precipitate and lost.

Separation from Boric Acid

Acidify the solution strongly with hydrochloric acid and evaporate to dryness. Stir up the residue with 15 to 20 cc. of pure methyl alcohol and cautiously evaporate on a water bath at not too high a temperature. Moisten the residue with a drop or two of concentrated hydrochloric acid, add 15 cc. of methyl alcohol, and again take to dryness. Repeat the evaporation with methyl alcohol a third time. This should be ample for the complete removal of half a gram of B_2O_3.

Separation from Magnesium

Mercuric Oxide Method.[1] After removing other bases and acids, evaporate the solution of the chlorides to dryness, expel ammonium chloride by gentle ignition, and dissolve the residue—except for the small amount of magnesium oxide present—by warming with a little water. Add an excess of mercuric oxide in the form of a thin paste prepared by shaking up freshly precipitated mercuric oxide in water. Evaporate the mixture to complete dryness on the water bath with frequent stirring, dry thoroughly and ignite gently at first and then more strongly until all the mercuric chloride present has been volatilized. (Be careful not to inhale the fumes.) The whole of the unchanged mercuric oxide need not be expelled by ignition. Digest the residue, composed of the excess of mercuric oxide, the precipitated magnesium oxide, and the alkali chlorides, with a small amount of hot water, filter rapidly, and wash with successive portions of hot water, first by decantation and then on the filter, but do not prolong the operation unnecessarily. If desired, determine the magnesium in the residue by expelling the mercuric oxide by ignition and weighing the magnesium oxide. Acidify the filtrate, which contains the alkalies, with hydrochloric acid, evaporate to dryness, gently ignite, cool and weigh. If the residue contains a small amount of magnesium, as it usually does, determine the magnesium in an aliquot and apply the necessary correction. The mercuric oxide should be tested for alkalies by volatilizing a portion and testing the residue.

The Barium Hydroxide Method.[1] Evaporate the solution, which may contain chlorides, sulphates or nitrates, to dryness and gently ignite to remove ammonium salts. Warm the residue with a small amount of water and treat the hot neutral solution so obtained with baryta water until no more precipitate is formed and barium hydroxide remains in slight excess. Boil, filter and wash

[1] Fresenius, "Quantitative Chemical Analysis," 1, 610, 1908, John Wiley & Sons, New York.

the precipitate with hot water. If desired, determine the magnesium in the residue. Treat the filtrate, which contains the alkalies, barium and a trace of magnesium, with an excess of ammonia and ammonium carbonate to remove the barium. Acidify the filtrate with hydrochloric acid and evaporate to dryness, ignite and weigh. This residue will contain a small amount of magnesium which may be determined in an aliquot and a correction applied.

Remark. The barium hydroxide method is applicable in the presence of lithium.

The Ammonium Phosphate Method.[1] To the hot solution, add an excess of ammonia and ammonium chloride, and precipitate the magnesium by adding a slight excess of ammonium phosphate. Allow the mixture to stand an hour or so, filter and wash the residue with 2% ammonia solution. Expel most of the free ammonia from the filtrate by evaporation, acidify very slightly with hydrochloric acid, and add an excess of ferric chloride solution, which should color the solution slightly yellow. Neutralize the solution with ammonium carbonate, heat to boiling, and filter off the basic ferric phosphate, washing the residue with hot water. Evaporate the filtrate to dryness, ignite to expel ammonium salts, and determine the alkalies in the residue. Magnesium may also be separated by precipitation as magnesium ammonium arsenate [2] or magnesium ammonium carbonate.[1]

Separation of the Alkali Metals from One Another

Separation of Sodium from Potassium

After weighing the sodium and potassium together as chlorides, dissolve the residue in water and precipitate the potassium as chloroplatinate or perchlorate according to one of the methods detailed under Determination of Potassium.

Separation of Lithium from Sodium and Potassium

Extract the dry chlorides with amyl alcohol as prescribed under the Gooch method, or with alcohol saturated with hydrochloric acid gas as detailed under the Rammelsberg method.

Separation of Lithium and Sodium from Potassium, Rubidium, and Caesium

Precipitate the potassium, rubidium, and caesium as chloroplatinates as described under the chloroplatinate method for the estimation of potassium. Evaporate the filtrate to dryness and ignite gently with a little oxalic acid to reduce the platinum, or else dissolve the residue in water and pass a current of hydrogen through the hot solution to reduce the platinum. In any case, filter off the reduced platinum and determine lithium and sodium in the filtrate.

[1] Fresenius, op. cit.
[2] Browning and Drushel, Am. J. Sci. (4), **23**, 293, 1907.

METHODS FOR DETERMINATION OF SODIUM

Determination as Sodium Chloride

Sodium is commonly weighed as NaCl when it is already present as such or after conversion of other forms into the chloride. In the case of salts of volatile acids, such as nitrates for instance, the transformation is made by evaporating the solution to dryness with hydrochloric acid repeatedly or until only the chloride remains. When the sodium is present as a salt of a non-volatile acid, the latter is removed and the transformation effected according to the methods under Separations.

Usually the solution in which sodium chloride is to be determined will contain ammonium salts from some previous operation. In such cases, proceed as follows: Evaporate the sodium chloride solution, which must contain no other non-volatile substance, in a platinum dish to complete dryness on the water bath. Cover the dish with a watch-glass, and cautiously dry the residue in an air bath at 110 to 130° C. Make sure that no loss of sodium chloride is sustained by decrepitation during drying and subsequent ignition. Heat the dish and contents over a free flame held in the hand and moved back and forth under the dish in order to remove ammonium salts. But to avoid loss of sodium chloride by volatilization, take care not to heat the dish to more than a faint redness in any one spot and not to raise the temperature of the salt above incipient fusion. Cool the residue, dissolve it in a little water, and filter from the carbonaceous matter into a weighed platinum dish. Acidify the filtrate with hydrochloric acid and evaporate it to dryness on the water bath. Dry the residue at 100 to 130° C. in an air bath, ignite cautiously over a free flame, taking the precautions mentioned above to prevent loss of sodium chloride, cool in a desiccator, and weigh.

Determination as Sodium Sulphate

Sodium is often determined by weighing as Na_2SO_4 when it is present as such or after conversion of other forms into the sulphate. In the case of salts of volatile acids, the change into the sulphate is made by simply evaporating the solution with a slight excess of sulphuric acid. With salts of non-volatile acids, the transformation is effected according to the methods under Separations. When the sodium is present as an organic salt, the substance is moistened with concentrated sulphuric acid and carefully heated over a free flame until fumes cease to come off. The residue is dissolved in water and filtered from the carbonaceous matter.

As a rule the solution in which sodium sulphate is to be determined will contain an excess of sulphuric acid. In such cases, evaporate the solution to dryness in a weighed platinum dish, and cautiously ignite the dry residue until fumes cease to come off. Cool, add a lump of ammonium carbonate to the contents of the dish, and ignite a second time at dull red heat until no more fumes are given off. Cool in a desiccator and weigh as Na_2SO_4. Repeat the ignition with the addition of ammonium carbonate until a constant weight is obtained.

In case an excess of sulphuric acid is not present, evaporate the solution to dryness in a weighed platinum dish, ignite, cool in a desiccator and weigh as Na_2SO_4.

Determination by Difference

Ordinarily sodium and potassium are weighed together as chlorides or sulphates as detailed above for sodium. Potassium is then determined by one of the methods given below, and the value for sodium obtained by difference.

METHODS FOR DETERMINATION OF POTASSIUM

Determination as Potassium Chloride or Potassium Sulphate

Potassium may be weighed as chloride or sulphate. The procedure is the same as that described for sodium. Observe, however, that the potassium salts are a little more volatile than the corresponding sodium salts, so that greater care must be taken not to lose potassium by volatilization.

The Chloroplatinate Method

Application. This method is applicable in the presence of the chlorides of sodium, lithium, magnesium, calcium, and strontium.

Principle. Potassium chloroplatinate is practically insoluble in strong alcohol while the other chloroplatinates are readily soluble.

Procedure. Treat the aqueous solution of the alkali chlorides contained in a small porcelain dish with slightly more than enough chloroplatinic acid to convert all the chlorides present into the corresponding chloroplatinates. The chloroplatinic acid solution should contain the equivalent of 1 gram of platinum in each 10 cc.[1] Evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. Pour the liquid through a previously weighed Gooch crucible containing an asbestos mat, and before adding more alcohol, rub up the residue again with the glass pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Transfer the precipitate to the crucible and wash two or three times with alcohol. Dry at 130° C., cool in a desiccator, and weigh. Repeat the drying until a constant weight is obtained. Multiply the weight of K_2PtCl_6 by 0.161 to obtain the weight of K; by 0.194 to obtain K_2O; and by 0.307 to obtain KCl.

Remarks. This method is considered to be the most accurate known for the estimation of potassium. Care should be taken not to conduct the evaporation at too high a temperature nor let it go too far, as this may cause the formation of anhydrous sodium chloroplatinate, which dissolves slowly in alcohol. Too large a volume of alcohol for washing should be avoided, as K_2PtCl_6 is slightly soluble in alcohol, especially that of 80%. For this reason 95% alcohol is preferable for the washing.

Instead of using a Gooch crucible, the precipitate may be filtered on paper, dried, washed through the filter with hot water into a weighed platinum dish, evaporated to dryness, and heated at 130° C. to constant weight.

[1] For methods of preparing chloroplatinic acid from scrap platinum and from platinum residues, see Precht, Z. Anal. Chem., 18, 509, 1879; Vogel and Haefcke, Landw. Vers. Sta., 47, 134, 1896.

The Modified Chloroplatinate Method [1]

Application. The method is applicable in the presence of chlorides, sulphates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and alumina, and is especially suited for the estimation of potassium in salines, potassium salts, and fertilizers in which only the potassium is desired.

Principle. On evaporating a solution containing potassium with a slight excess of chloroplatinic acid, the potassium is completely transformed into potassium chloroplatinate which is insoluble in strong alcohol, while any of the other chloroplatinates which may be formed are either dissolved or decomposed by alcohol, so that the excess of chloroplatinic acid may be readily removed. After dissolving the K_2PtCl_6 along with any other soluble salts contained in the residue in hot water, the platinum is precipitated from the solution by magnesium, and from the weight of platinum so obtained, the amount of potassium present is calculated.

Procedure. To the solution slightly acidified with hydrochloric acid, add chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chloroplatinic acid has been used. Pour the liquid through a small filter, using suction if desired, and before adding more alcohol, rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate of K_2PtCl_6 along with any other soluble salts present in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 1 cc. of concentrated HCl and approximately 0.5 gram magnesium ribbon pressed into the form of a ball for every 0.2 gram potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. When the action has practically ceased, add a few cc. of hydrochloric acid and allow the fluocculent platinum to settle, preferably by allowing the beaker to set for an hour on the hot plate. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure, add more magnesium, in which case the solution will darken if reduction be incomplete. To the completely reduced solution, add concentrated hydrochloric acid, and boil to dissolve any basic salts, filter on paper or a Gooch, wash thoroughly with hot water, ignite in platinum or porcelain and weigh. Multiply the weight of the platinum so obtained by 0.4006 to obtain the weight of K; by 0.4826 to obtain K_2O; and by 0.7639 to obtain KCl.

Remarks. If the solution contains very large amounts of iron, alumina, or silica, it is perferable to remove the greater part of these before proceeding to the determination of potassium. Care should be taken to insure the complete removal of the soluble chloroplatinates from the residue without the use of an

[1] Hicks, J. Ind. Eng. Chem., 5, 650, 1913. A good bibliography on reduction methods is contained in this article.

xcessive amount of alcohol, and also that the subsequent reduction of the potassium chloroplatinate with magnesium be complete.

Lindo-Gladding Method [1]

Application. This method is applicable in the presence of chlorides, sulhates, and phosphates of the alkalies and magnesium.

Principle. The potassium is precipitated as K_2PtCl_6, and the soluble chloroatinates removed by washing with 80% alcohol. The impurities in the precipate are then washed out by a strong solution of ammonium chloride saturated ith K_2PtCl_6, and the wash solution is removed by again washing with alcohol. he purified K_2PtCl_6 is finally dried and weighed.

Procedure. To the solution, slightly acidified with hydrochloric acid, add n excess of chloroplatinic acid solution, and evaporate on the water bath to a thick aste. Treat the residue with 80% alcohol, avoiding the absorption of ammonia. Wash the precipitate thoroughly with 80% alcohol both by decantation and on ie filter, continuing the washing after the filtrate is colorless. Wash finally ith 10 cc. of ammonium chloride solution prepared as follows: Dissolve 100 rams of pure ammonium chloride in 500 cc. of water, add from 5 to 10 grams of otassium chloroplatinate, and shake at intervals of six to eight hours. Allow ie mixture to settle over night and filter. Repeat the washing with successive ortions of the ammonium chloride solution five or six times in order to remove ie impurities from the precipitate. Wash again thoroughly with 80% alcohol, ry for thirty minutes at 100° C. and weigh as K_2PtCl_6. The precipitate should e perfectly soluble in water. Multiply the weight of K_2PtCl_6 by 0.161 to obtain ie weight of K; by 0.194 to obtain K_2O; and by 0.307 to obtain KCl.

The Perchlorate Method [2]

Application. This method is applicable in the presence of chlorides and itrates of barium, calcium, magnesium and the alkali metals, and also in the resence of phosphates. Sulphates should not be present.

Principle. The separation depends on the insolubility of potassium perchlorte, and the solubility of sodium and other perchlorates in 97% aclohol.

Procedure. To the neutral or slightly acidified solution, add twice as much perchloric acid [3] as is required to convert all the bases present into perchlorates and evaporate on the water bath with stirring to a syrupy consistency. Add a little hot water and continue the evaporation with constant stirring until all the hydrochloric acid is expelled and heavy fumes of perchloric acid are given off. If necessary, replace the perchloric acid lost by volatilization. Stir up the cooled mass thoroughly with 20 cc. of 97% alcohol to which 0.2% perchloric acid has been added, but avoid breaking up the potassium perchlorate crystals too finely or else they may pass through the filter. Allow the mixture to settle, and decant the alcohol off through a Gooch crucible. Wash several times with wash-alcohol, and transfer the precipitate to the filter. Wash with 50 to 75 cc. of pure 97% alcohol, dry at 130° C., and weigh. Multiply the weight of $KClO_4$ by 0.2825 to obtain the weight of K; by 0.3402 to obtain K_2O; and by 0.5382 to obtain KCl.

[1] U. S. Dept. Agri., Bu. Chem. Bull. 107 (revised), **11**, 1907.

[2] Wense, Zeit. Angew. Chem., 691, 1891; 233, 1892. Caspari, Zeit. Angew, Chem., 68, 1893.

[3] For the preparation of perchloric acid see Willard, J. Am. Chem. Soc., **34**, 1480, 1912; Kreider, Am. J. Sci., (3), **49**, 443, 1895. 3. Anorg. Chem., **9**, 342, 1895.

Other Methods

Among the more important of other methods which have been proposed and used for the determination of potassium, may be mentioned the cobaltinitrite method,[1] which has been studied by the Association of Official Agricultural Chemists and considered to be unreliable;[2] the bitartrate method;[3] the colorimetric method;[4] and the spectroscopic method.[5]

Determination of Sodium and Potassium by Indirect Method

After removing all other constituents, weigh the sodium and potassium as chlorides. Dissolve the weighed residue in water and determine the chlorine gravimetrically by precipitation as AgCl or volumetrically by titration with standard silver nitrate (potassium chromate indicator). From the weight of the combined salts and the weight of the chlorine, calculate the amount of sodium and potassium as follows:

Let x = weight of NaCl+KCl.
y = weight of Cl.
Then $\text{Na} = 3.004y - 1.428x$;
$\text{K} = 2.428x - 4.004y$.

The method is satisfactory when sodium and potassium are present in about equal quantities.

Determination of Magnesium, Sodium and Potassium in the Presence of One Another

In the usual course of analysis, magnesium, sodium and potassium are separated as chlorides from all other constituents. Instead of going through the tedious process of separating the magnesium from the alkalies, the magnesium, sodium, and potassium may be accurately determined in the presence of each other as follows:

Treat the solution containing these constituents with slightly more than enough sulphuric acid to convert all three bases into sulphates, evaporate it to dryness on the water bath, and ignite gently at first and then at dull red heat to break up bisulphates and expel the excess of sulphuric acid. To hasten the decomposition of the bisulphates, cool, add a lump of ammonium carbonate, and heat a second time. Cool in a desiccator and weigh. Repeat the heating with the addition of ammonium carbonate until a constant weight is obtained. Dissolve the residue in water and dilute to definite volume. Determine the potassium in one portion according to one of the methods described above, and the magnesium in a second portion as described on page 255. Deduct the weight of magnesium and potassium sulphates from the weight of the combined sulphates to obtain the amount of sodium sulphate.

[1] Addie and Wood, J. Chem. Soc., **77**, 1076, 1900; Drushel, Am. J. Sci. (4), **24**, 433, 1907; **26**, 329, 555, 1908; Bowser, J. Am. Chem. Soc., **33**, 1752, 1911.
[2] U. S. Dept. Agri. Bu., Chem., Bull. 132, 137, 152, 159.
[3] Bayer, Chem. Zeit., **17**, 686, 1893.
[4] Cameron and Failyer, J. Am. Chem. Soc., **25**, 1063, 1903; Hill, J. Am. Chem. Soc., **25**, 990, 1903.
[5] Gooch and Hart, Am. J. Sci. (3), **24**, 448, 1891.

METHODS FOR DETERMINATION OF LITHIUM

Determination as Lithium Chloride

Lithium may be weighed as LiCl. The procedure is practically the same as that described for sodium, but since lithium chloride is very hygroscopic, this salt must be weighed out of contact with the air. For this purpose the lithium chloride is ignited in a platinum crucible, cooled in desiccator, and the crucible and contents weighed in a glass-stoppered weighing bottle.

Determination as Lithium Sulphate

Lithium is weighed preferably as Li_2SO_4. The procedure is the same as that described for sodium, but since lithium bisulphate is easily broken up on heating, it is not necessary to ignite with ammonium carbonate.

The Gooch Method [1]

Principle. Lithium chloride is readily soluble in amyl alcohol, while sodium and potassium chlorides are not.

Procedure. Concentrate the solution as far as possible by evaporation, transfer it to a 50-cc. Erlenmeyer flask, add a small amount of amyl alcohol and heat cautiously on an asbestos plate until the water has been expelled and the boiling-point of the solution rises to about that of pure amyl alcohol (132° C.). To prevent bumping during this treatment, pass a current of dry air through the solution. When all the water has been removed, the sodium and potassium chlorides, together with some LiOH will separate from the solution. Decant the solution through a filter and wash the residue several times with hot amyl alcohol. Moisten the residue with dilute hydrochloric acid, dissolve in a little water and repeat the extraction with amyl alcohol. If much lithium chloride is present, it will be necessary to repeat the extraction with amyl alcohol three or four times. Evaporate the combined filtrates and washings to dryness and dissolve in a little dilute sulphuric acid. Filter from the carbonaceous matter into a weighed platinum dish, evaporate to dryness, and remove the excess of sulphuric acid by gentle heating. Ignite the residue at dull redness, cool in a desiccator, and weigh as Li_2SO_4.

Remarks. For very accurate work, account must be taken of the fact that the lithium sulphate obtained according to the procedure just described always contains small amounts of potassium and sodium sulphates, if these metals were originally present. To correct for this, deduct 0.00041 gram for every 10 cc. of the filtrate exclusive of the washings in case only sodium chloride was present, or 0.00051 if only potassium chloride was present, and 0.00092 if both sodium and potassium chlorides were present.

[1] Proc. Am. Acad. Arts. Sci., 22 (N. S. 14), 177, 1886.

The Rammelsberg Method [1]

Principle. Anhydrous lithium chloride is soluble in equal parts of alcohol and ether which have been saturated with hydrochloric acid gas, while the chlorides of sodium and potassium are practically insoluble in this mixture.

Procedure. Evaporate the solution of the chlorides to dryness in a small flask provided with a two-hole stopper. During the evaporation, pass a current of dry air through the flask. Place the flask containing the dry residue in an oil or air bath and heat for half an hour at 140 to 150° C., during which time pass dry hydrochloric acid gas through the flask. Cool in a current of hydrochloric acid gas, treat the residue with a few cc. of absolute alcohol which has been saturated with hydrochloric acid gas, and add an equal volume of absolute ether. Close the flask tightly and allow it to stand with frequent shaking for twelve hours. Pour the solution through a filter, wet with the alcohol-ether mixture and wash the residue three times by decantation with the alcohol-ether mixture. Add a few more cc. of the alcohol-ether saturated with hydrochloric acid gas to the contents of the flask and allow to stand again for twelve hours. Pour the liquid through a filter, and wash the residue by decantation with the alcohol-ether mixture until the residue tested in the spectroscope shows the complete absence of lithium. Carefully evaporate the combined alcohol-ether extract to dryness on a lukewarm water bath. Dissolve the residue in sufficient dilute sulphuric acid to convert all the lithium into the sulphate, transfer the solution to a weighed platinum dish, evaporate to dryness on the water bath, and finally ignite gently. Cool the residue in a desiccator and weigh as lithium sulphate.

NOTE. Lithium may also be precipitated and weighed as Li_3PO_4,[2] or it may be precipitated as LiF [3] and then changed into the sulphate and weighed.

Spectroscopic Method [4]

Dissolve the lithium salt containing small amounts of sodium and potassium resulting from the separation by the Gooch or Rammelsberg methods in 5 or 10 cc. of water, depending on the amount of lithium present. Gradually add measured amounts of this solution to a known volume of water—testing the solution from time to time in the spectroscope—until the lithium line appears. When only traces of lithium are present, it is better to dissolve the lithium salt in a little water and dilute to the vanishing point of the lithium line. Make the spectroscopic examination as follows: Prepare a loop by winding a platinum wire four times around a No. 10 wire. Plunge the loop into the solution, and remove with the axis parallel to the surface of the water. Evaporate the drop to dryness carefully, ignite in the Bunsen flame, and observe through a good spectroscope.

Before undertaking the determination, standardize the instrument and platinum loop by carrying out the determination with known amounts of lithium.

The method gives satisfactory results when only an approximation is desired. For weighable amounts of lithium, the Gooch method is preferable.

[1] Treadwell, "Analytical Chemistry," 2, 55, 1911. John Wiley & Sons, N. Y.
[2] Mayer, Ann. Chem. Pharm., 98, 193, 1856. Merling, 3 Anal. Chem., 18, 563, 1879.
[3] Carnot, 3 Anal. Chem., 29, 332, 1890.
[4] Skinner and Collins, U. S. Dept. Agri. Bu. Chem., Bull. 153. A good bibliography is included in this bulletin.

Determination of Sodium, Potassium, and Lithium in the Presence of One Another

Weigh the combined bases as sulphates, observing the precautions detailed under Determination of Sodium, dissolve in water and dilute to definite volume. In one portion determine the potassium and in a second portion determine the lithium by the Gooch or Rammelsberg method. Obtain the value for the sodium by difference.

Determination of the Alkalies in Silicates

J. Lawrence Smith method [1]

Principle. By heating the substance with 1 part ammonium chloride and 8 parts calcium carbonate, and leaching the sintered mass with water, the alkalies are obtained in solution in the form of chlorides along with some calcium, while the remaining metals are for the most part left behind as insoluble oxides, and the silica is changed to calcium silicate.

Procedure. Triturate 0.5 gram of the finely powdered mineral with an equal quantity of pure ammonium chloride in an agate mortar, add 3 grams of precipitated calcium carbonate [2] and mix intimately with the former. Transfer the mixture to a platinum crucible (preferably the J. Lawrence Smith alkali crucible), rinse the mortar with 1 gram of calcium carbonate and add to the contents of the crucible. Place the covered crucible in a slightly inclined position with the top protected from the heat of the flame This can be done by setting the crucible in a hole in a cylinder of fire clay, as shown in Fig. 56. Gradually heat the crucible over a small flame until no more ammonia is evolved, but avoid heating sufficiently to cause the evolution of ammonium chloride. This should require about fifteen minutes. Then raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a red heat, and maintain this temperature for one hour. Allow the crucible to cool and remove the sintered cake by gently tapping the inverted crucible. Should this not be possible, digest the mass a few minutes with water to soften the cake, and then wash it into a large porcelain or platinum dish. Heat the covered dish with 50 to 75 cc. of water for half an hour, reduce the large particles to a fine powder by rubbing

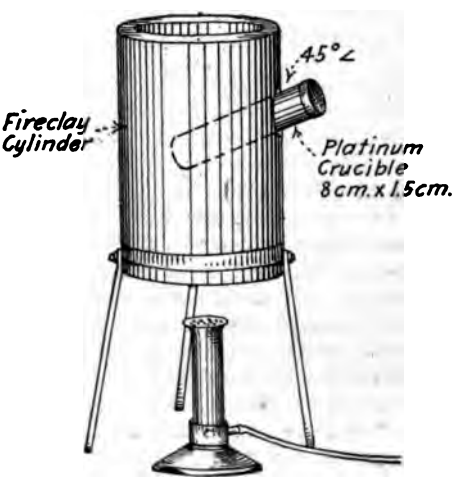


FIG. 56.

[1] Am. J. Sci. (3), 1, 269, 1871; Hillebrand, U. S. Geol. Survey Bull. 422, 171, 1910.

[2] Blank determinations should be run on the calcium carbonate, and corrections made for its alkali content.

with a pestle in the dish, and decant the clear solution through a filter. Wash the residue four times by decantation, transfer it to a filter, and wash with hot water until a few cc. of the washings give only a slight turbidity with silver nitrate. To make sure the decomposition of the mineral has been complete, treat the residue with hydrochloric acid. No trace of undecomposed mineral should remain undissolved.

The aqueous extract obtained in the above operation contains the chlorides of calcium and the alkalies. To remove the calcium, treat the solution with ammonia and ammonium carbonate, heat to boiling, filter and wash the residue. As this precipitate invariably retains some alkali salts, it should be dissolved in hydrochloric acid and the precipitation repeated. Evaporate the filtrate to dryness in a platinum or porcelain dish, and expel the ammonium salts by gentle ignition over a moving flame. After cooling, dissolve the residue in a little water, and add a few drops of ammonia and ammonium oxalate to remove the last trace of calcium. After standing several hours, filter off the calcium oxalate, receive the filtrate in a weighed platinum dish, evaporate to dryness and ignite gently to remove ammonium salts. Moisten the cooled mass with hydrochloric acid to transform any carbonate into chloride, and again evaporate to dryness and ignite. Cool in a desiccator and weigh the combined chlorides. Dissolve in water, and if an insoluble residue remains, filter off, weigh and deduct from the weight of the chlorides. Determine the potassium by one of the methods already described, and obtain the value for sodium by difference.

The Hydrofluoric Acid Method[1]

Procedure. Weigh about 0.5 gram of the finely powdered mineral into a platinum dish, add 3 or 4 cc. of dilute sulphuric acid, and stir up the mixture with a platinum rod. After cooling, add about 5 cc. of pure concentrated hydrofluoric acid, and evaporate the solution on the water bath, frequently stirring with the platinum rod, until the hydrofluoric acid is expelled and no more hard particles can be felt at the bottom of the dish. Volatilize the greater part of the sulphuric acid by heating to make sure of the complete removal of the hydrofluoric acid, but do not remove all the sulphuric acid in order to avoid the formation of insoluble basic salts. Cover the cooled mass with 200 cc. of water, and digest until all the residue has gone into solution. Precipitate the sulphate by addition of a slight excess of barium chloride solution, and without filtering off the barium sulphate, precipitate the aluminum, calcium and excess of barium by treatment with ammonia and ammonium carbonate. Allow the precipitate to settle, filter, wash four times by decantation and then on the filter until free from chlorides. Evaporate the filtrate to dryness, and remove the ammonium salts by gentle ignition. Dissolve the residue in a little water, and separate the magnesium according to one of the methods described above. Finally weigh the alkalies as chlorides or sulphates. Determine the potassium in the residue and obtain the value for sodium by difference.

Determination of the Alkalies in Alunite

Thoroughly mix the finely powdered mineral with an equal weight of pure silica, and proceed as directed under the J. Lawrence Smith method for the

[1] Treadwell, op. cit., p. 499.

determination of the alkalies in silicates. In this case, however, the water extract will contain a large amount of sulphate, which should be removed by precipitation with barium chloride solution before undertaking to separate the calcium.

For an approximate determination, ignite a half gram of the powdered mineral for an hour or so at low red heat, cool, leach out with water, evaporate to dryness, and weigh the residual sulphates. If sodium is present, determine the potassium in the residue.

Determination of the Alkalies Volumetrically

Titration with Standard Acid

When sodium or potassium is present as a hydroxide or salt of a weak acid such as carbonate or borate, either metal when present alone may usually be determined by titration with standard acid and methyl orange.

Titration with Standard Silver Nitrate

The alkalies may be determined when present alone as chloride by titration with standard silver nitrate, potassium chromate indicator.

SELENIUM AND TELLURIUM

WILFRED W. SCOTT

Se, *at.wt.* 79.2; *sp.gr.* { *amorphous* 4.26; *m.p.* 217°; / *crystalline* 4.82; } *b.p.* 690° C.; *oxide* SeO_2; *acids*, H_2SeO_3, H_2SeO_4.

Te, *at. wt.* 127.5; *sp.gr.* 6.27; *m.p.* 452°;[1] *b.p.* 1390° C.; *oxides* TeO, TeO_2, TeO_3; *acids*, H_2TeO_3, H_2TeO_4.

DETECTION

Selenium and tellurium appear with the hydrogen sulphide subgroup elements in the ordinary course of qualitative analysis. The acid solution of the material is treated cold with H_2S, as the lemon-yellow SeS, formed in a cold solution is more readily soluble in alkaline sulphide solutions than the orange-yellow SeS_2 precipitated from hot solutions. Although only a partial separation takes place the extract will contain sufficient selenium, if present in the sample, to give a qualitative test. By precipitation from an acid solution by H_2S, selenium and tellurium are separated from members of subsequent groups. The sulphides precipitated are extracted with sodium or ammonium sulphide and the extract examined for selenium and tellurium.

Detection of Selenium

The sodium or ammonium extract is acidified with hydrochloric acid, whereby selenium together with the other members of the group are precipitated. The washed dried precipitate is mixed with twice its weight of a flux containing equal parts of sodium carbonate and nitrate, and the mixture added to an equal amount of the flux which has been previously fused. The fluid mass is poured on to a slab of porcelain and the cooled melt placed in a beaker and extracted with water, whereby selenic, telluric, molybdic and arsenic acids dissolve, stannic oxide, sodium antimonate, gold and the platinum group remaining insoluble. The extract is treated with an excess of hydrochloric acid and boiled to reduce sodium selenate, Na_2SeO_4, to selenious acid, H_2SeO_3. A reducing agent such as sulphurous acid, ammonium sulphite, hydrazine sulphate or hydroxylamine is added and the solution boiled. Selenium, if present, is precipitated in its red or brown colored metallic form. The red color darkens on boiling.

Selenium is an odorless and tasteless solid. *Its vapor* has a putrid horseradish odor. The element burns with a reddish-blue colored flame.

Dissolved in *concentrated sulphuric acid* a fine green-colored solution is obtained, from which solution selenium may be precipitated by dilution with water, the suspended substance giving a reddish tint to the acid.

[1] Circular 35 (2d Ed.), U. S. Bureau of Standards.

Hydrochloric acid decomposes selenates with evolution of chlorine gas on boiling.

Barium.chloride precipitates white $BaSeO_3$, soluble in dilute HCl, when added to selenites, and white $BaSeO_4$, insoluble in dilute HCl, when added to selenates.

Hydrogen sulphide produces no precipitate with a selenate. This reduced, however, by heating with HCl, a lemon-yellow to orange-yellow precipitate of SeS_2 is obtained.

The gas passed into a solution of selenite gives an immediate precipitation of the sulphide, SeS_2.

Detection of Tellurium

Tellurium dissolved in *concentrated sulphuric acid* colors the acid purple or carmine. The color disappears on dilution. The mineral may be treated directly with hot concentrated sulphuric acid and the color obtained in presence of tellurium.

Heated in a test-tube tellurium compounds sublime and fuse to colorless, transparent drops of TeO_2.

Hydrogen sulphide precipitates metallic tellurium mixed with sulphur when passed into acid solutions containing the element. The precipitate resembles SnS in appearance. It is readily soluble in $(NH_4)_2S$.

Tellurium *burns* with a greenish flame.

Reducing agents added to acid solutions of tellurium precipitate black metallic tellurium.

Tellurium compounds are not as readily reduced as are those of selenium. In solutions having an acidity of over 80 per cent, SO_2 gas causes the precipitation of metallic selenium alone. Upon dilution with an equal volume of water tellurium is precipitated. A separation may be effected in this way.

Tellurates *boiled with HCl* evolve chlorine gas and are reduced to H_2TeO_3. Dilution of the solution will cause the precipitation of TeO_2 (distinction from Se).

Potassium iodide added to a tellurite in dilute sulphuric acid solution (1 : 4) precipitates black TeI_4, soluble in excess of KI.

ESTIMATION

Selenium and tellurium closely resemble sulphur in chemical properties. They have crystalline and amorphous forms. The elements occur in nature frequently associated with sulphur. Selenium is frequently present in iron pyrites, hence is found in the flue dust of lead chambers of the sulphuric acid plant, and as an impurity in sulphuric acid, prepared from pyrites containing selenium.

Ores—Selenium. In copper and iron pyrites; meteoric iron. In the rare minerals clausthalite, PbSe; lehrbachite, PbSe·HgSe; onofrith, HgSe·4HgS; eucairite, CuSe·Ag_2Se; crookesite, (CuTlAg)Se.[1]

Tellurium. Occurs in tellurides and arsenical iron pyrites. Frequently associated with gold, silver, lead, bismuth and iron. In the minerals—altaite, PbTe; calaverite, $AuTe_2$; coloradolite, HgTe; nagyagite, $(AuPb)_2(TeSSb)_2$; petzite, Ag_2AuTe_2; sylvanite, $AuAgTe_4$; telluride, TeO_2 (tellurium ochre); tetradymite, Bi_2Te_3.[1]

[1] Thorpe, " Dictionary of Applied Chemistry."

Preparation and Solution of the Sample

The following facts regarding solubilities of these elements and their compounds may be useful in the analysis of these substances.

Selenium. Amorphous selenium is soluble in carbon disulphide; the crystalline hexagonal form is insoluble in this reagent. The metal is soluble in hydrochloric acid in the presence of nitric acid. It is soluble in cold concentrated sulphuric acid, giving a green-colored liquid, which diluted with water deposits selenium. The dioxide, SeO_2, is readily soluble in hot water.

Tellurium. The element dissolves in hot concentrated hydrochloric acid. On dilution of the solution a precipitation of $H_2TeO_3 \cdot TeO_3$ occurs. Treated with concentrated nitric acid or aqua regia H_2TeO_4 forms. With sulphuric acid the compound H_2TeO_3 forms and SO_2 is evolved. The element dissolves in concentrated potassium cyanide, from which solution hydrochloric acid precipitates all of the tellurium. Tellurium is insoluble in carbon disulphide. The oxides TeO and TeO_2 are soluble in acids, TeO_3 being not readily soluble. All the oxides dissolve in hot potassium hydroxide solutions.

Care must be exercised to avoid overheating acid extracts in the preparation of the sample, since loss by volatilization is apt to occur; this is especially true of the halogen compounds of selenium and tellurium, the former being more volatile than the latter. (B.p. $SeCl_2 = 145°$; $Se_2Br_2 = 225° - 230°$; $SeOCl_2 = 179.5°$; $TeCl_2 = 327°$; $TeCl_4 = 414°$; $TeBr_2 = 339°$; $TeBr_4 = 420°$ C.)[1]

Fusion Method. The finely powdered substance is intimately mixed with about five times its weight of a flux of sodium carbonate and nitrate (4 : 1) and heated gently in a nickel crucible, gradually increasing the heat, until the charge has fused. When the molten mass appears homogeneous, it is cooled and extracted with water. Sodium selenate and tellurate pass into solution and are separated from most of the heavy metals. The water extract is acidified with hydrochloric acid and boiled until no more free chlorine is evolved. (Test with starch iodide paper. Cl = blue color.)[2] Metallic selenium and tellurium may be precipitated by passing sulphur dioxide into the hydrochloric acid solution.

Keller has shown that tellurium is not precipitated by SO_2 in strong hydrochloric acid solutions (sp.gr. 1.175), whereas selenium is precipitated. Diluted with an equal volume of water (acidity 30 to 50% of above) both tellurium and selenium are precipitated by SO_2.

SEPARATIONS

One or more of the following procedures may be required according to the material that is being analyzed.

Separation of Selenium and Tellurium from the Iron and Zinc Groups, from the Alkaline Earths and the Alkalies. If sulphur dioxide is passed into a solution containing 30 to 50% of hydrochloric acid (sp.gr. 1.175), selenium and tellurium will be precipitated, the other elements remaining in solution. If the acidity is over 80% of the above strength of hydrochloric acid, only selenium is precipitated.

[1] Van Nostrand's Chem. Annual.

[2] According to B. Rathke, Zeit. anal. Chem., 9, 484, 1870, no appreciable loss of elenium occurs in the presence of sodium or potassium chlorides. Rose claims that n appreciable loss occurs when solutions of selenlum are heated above 100° C.

The presence of nitric and of sulphuric acid prevents the copmlete precipitation of tellurium.

Separation of Selenium and Tellurium from Cadmium, Copper and Bismuth. Sulphur dioxide passed into an acid solution containing 30 to 50% hydrochloric acid (sp.gr. 1.175) precipitates selenium and tellurium free from cadmium, and the greater part of bismuth, copper, antimony, etc. Complete separation of selenium and tellurium may be effected by the distillation process described under Separation of Selenium and Tellurium, see below.

Separation from Silver. Silver is precipitated as the chloride, AgCl, selenium and tellurium remaining in solution.

Separation from Gold. The slightly acid solution, free from nitric acid, is diluted with water, ammonium oxalate or oxalic acid added and the precipitated gold allowed to settle several hours (preferably twenty-four hours or more). The gold is filtered off and the selenium and tellurium precipitated in the filtrate with sulphur dioxide.

In the absence of selenium, gold may be separated from tellurium by precipitation with ferrous sulphate added to the solution strongly acidified with hydrochloric acid. Tellurium remains in solution. (Selenium is also precipitated with ferrous sulphate.)

Separation of Selenium from Tellurium by Direct Precipitation, with Sulphur Dioxide in Strong Hydrochloric Acid Solutions—Keller's Method. The procedure has already been mentioned. Advantage is taken of the fact that tellurium is not precipitated by SO_2 in strong hydrochloric acid solutions, whereas selenium is precipitated.

Procedure. The two elements are precipitated by sulphur dioxide from an acid solution containing 30 to 40% of strong hydrochloric acid. The precipitate is dissolved in nitric acid and the solution evaporated to dryness on the steam plate. The residue is treated with 200 cc. of hydrochloric acid (sp.gr. 1.175) and boiled to free the solution of nitric acid, since the presence of this acid prevents complete precipitation of tellurium. A little sodium chloride is previously added to minimize the loss through volatilization during the heating. The hot solution is saturated with sulphur dioxide, whereupon selenium is quantitatively precipitated and may be filtered off, washed with a 90% solution of strong hydrochloric acid (sp.gr. 1.175, i.e., 9 parts HCl to 1 part by volume H_2O), followed by dilute acid, then by water until free of acid, and finally by alcohol. Weigh as metallic selenium after drying at 105° C. The tellurium is precipitated from the filtrate by diluting this with an equal volume of water, heating to boiling and again saturating with sulphur dioxide. The precipitate is washed with dilute hydrochloric acid (1 : 1), followed by water and alcohol, then dried and weighed as tellurium.

Separation of Selenium and Tellurium. Distillation Method

The following method is excellent for determining selenium and tellurium in alloys.

Procedure. The apparatus having been set up as is shown in the cut, Fig. 57, 0.5 gram of the alloy containing selenium and tellurium is placed in the distilling flask *D* and 30 cc. of H_2SO_4 (sp.gr. 1.84) added. All connections are made tight.

A current of dry HCl gas is allowed to flow into the distilling flask and the contents of the flask heated to 300° C. (The H_2SO_4 should not fume and the temperature should be kept below the boiling point of this acid, otherwise the

acid distilling into the reservoir *R* would interfere with the precipitation of selenium by SO_2.) Selenium distills as selenium chloride into *R*, while tellurium remains in the distillation flask. During the distillation, SO_2 gas is passed into *R*, to reduce the selenic salt in solution and precipitate metallic selenium.

The distillation is continued for two or three hours, keeping the temperature of the distillation flask at about 300° C. (i.e., below the boiling-point of H_2SO_4). The contents of the receiver *R* is transferred to a 400-cc. beaker, and the distillation continued into fresh HCl to assure complete volatilization of selenium from the flask *D*. The contents of the receiver and any of the metal adhering to the glass wool, or the glass of the vessel, are combined. (The adhering selenium is dissolved off with a little Bromine-Potassium Bromide solution.)

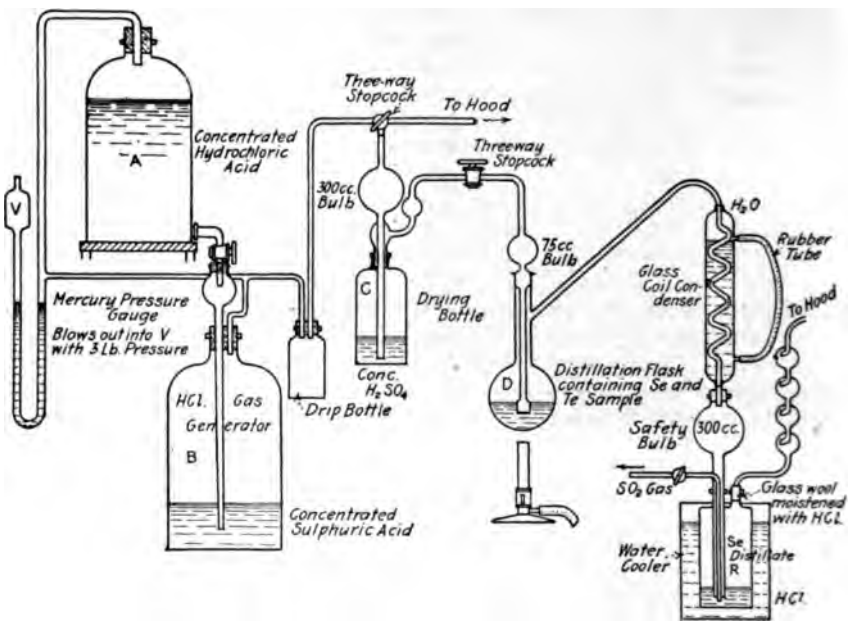


FIG. 57.—Apparatus for Determining Selenium and Tellurium.

Fig. 57 shows a convenient apparatus for routine determinations of selenium and tellurium in alloys. Hydrochloric acid gas is generated by allowing strong hydrochloric acid to flow into concentrated sulphuric acid (see *A* and *B* in drawing Fig. 57). The gas is dried by passing it through strong sulphuric acid (*C* in figure). A mercury pressure gauge, arranged to allow gas to blow out at a pressure of 3 or 4 pounds, prevents accident occurring due to stoppage in the system.

Determination of Selenium. The solution in the beaker is saturated with SO_2, then heated to boiling and the precipitated selenium allowed to settle several hours, or overnight. The precipitate is filtered into a weighed Gooch crucible, then washed with hot water and finally with alcohol. The residue is dried for an hour at 100° C. and weighed.

$$\frac{\text{Weight of Se} \times 100}{0.5} = \% \text{ Se.}$$

Determination of Tellurium. The residue in the distilling flask is transferred to a 600-cc. beaker containing 150 cc. of cold water. Ten cc. of 3% $Fe(NO_3)_3$ solution is added, and made ammoniacal, and then heated to boiling; the precipitate filtered off on a large filter and washed with hot water. The precipitate is dissolved in hot dilute HCl and the solution nearly neutralized with NH_4OH. The slightly acid solution is saturated with H_2S, the precipitated tellurium filtered off on an S. and S. No. 589, 12½ cm. filter, and washed with H_2S water.

The precipitate is dissolved off the paper into a small beaker with a mixture of equal parts of HCl and bromine-potassium bromide solution.[1] The paper is washed with water keeping the volume of the solution as small as possible. The filtrate should contain 20% HCl.

Tellurium is precipitated by saturating the solution with SO_2. The precipitate, after heating to boiling, is allowed to settle for several hours and filtered onto a weighed Gooch. It is washed with hot water and then with alcohol and dried for an hour at 100° C., cooled in a desiccator and weighed.

$$\frac{\text{Weight of Te} \times 100}{0.5} = \%\text{Te.}$$

GRAVIMETRIC METHODS FOR DETERMINING SELENIUM AND TELLURIUM

The sections on Preparation and Solution of the Sample and Separations should be carefully studied, as details for the precipitation of selenium and tellurium are given.

SELENIUM

Precipitation of Selenium by Sulphur Dioxide

The procedure for isolation of selenium by precipitation with sulphur dioxide gas, passed into the hydrochloric acid solution, has been given already in detail. For matter of convenience the procedure is briefly outlined here.

Procedure. The sample obtained in solution according to the procedure outlined under Preparation and Solution of the Sample and freed from nitric acid, is saturated with sulphur dioxide, whereupon selenium is precipitated in its elemental condition. If the solution is strongly acid with hydrochloric acid (HCl = sp.gr. 1.175), tellurium remains in solution, if present. It is advisable to wash the precipitated selenium with moderately strong hydrochloric acid, followed by the dilute acid, then with water until free of acid, and finally with alcohol. The residue is dried at 105° C. and weighed as metallic selenium.

The filtrate should be tested for selenium by saturating again with SO_2. Tellurium precipitates quantitatively from hydrochloric acid solution of half the above strength, hence will be evident in the filtrate, if present.

[1] The potassium bromide solution is made by adding 200 cc. of liquid bromine to 320 grams of potassium bromide salt dissolved in just sufficient water to form a saturated solution.

Reduction to Metallic Selenium Potassium Iodide Method

The method worked out by Peirce [1] is useful in determining selenium in samples containing less than 0.1 gram selenium. Larger amounts are apt to occlude iodine, giving high results.

Procedure. The sample containing selenious acid or a selenite is diluted to 400 cc. and acidified with hydrochloric acid. Potassium iodide is added in excess, about 3 grams more than is required to effect reduction, and the solution boiled about twenty minutes. The precipitate is filtered and washed as usual, then dried and weighed as metallic selenium.

TELLURIUM

Precipitation of Tellurium by Sulphur Dioxide

The procedure has been given under the section on Separations. The following method is useful for determining tellurium in samples in which selenium estimations are not desired.

Procedure. A sample of 1 to 5 gramsis taken for analysis and placed in a No. 5 porcelain crucible. Ten cc. of conc. HNO_3 are added very cautiously and, when the apparent action has ceased, the sample is placed on the steam bath until all NO_2 fumes have been expelled. Four to 5 drops of conc. H_2SO_4 are now added and the solution evaporated to dryness on the steam bath. About 15 cc. of conc. HCl are added and the solution again evaporated to dryness. By this latter procedure any selenium that may be present is converted to the easily volatile chloride. The crucible is placed on a triangle on a wire gauze over a low flame and heated cautiously [2] until all white fumes have disappeared and then at dull red heat until all signs of crystallized selenious chloride have disappeared. The residue in the crucible is tellurious dioxide and ferric oxide.

The crucible is cooled and the residue dissolved in conc. HCl in a No. 4 beaker and the solution diluted to 250 cc. with distilled water. H_2S is passed into the solution until tellurium is completely precipitated. The precipitate is filtered onto a 12½ cm. filter, S. & S. 589 quality, and washed with H_2S water.

The precipitate is dissolved in a 250-cc. beaker by adding a mixture of bromine-potassium bromide (200 cc. of liquid bromine added to 320 grams of KBr salt that has been dissolved in just sufficient water to form a saturated solution), 1 part and conc. HCl, 1 part, using the least amount of the mixture necessary to dissolve the precipitate and wash with a little water. The filtrate should contain 20% HCl.

The solution is thoroughly saturated with SO_4 gas, and then heated to boiling. The precipitated tellurium is allowed to settle for several hours, preferably over night, and filtered into a weighed Gooch crucible, then washed with hot water and finally with alcohol. After drying for an hour at 100° C., the tellurium is cooled and weighed.

Weight of the residue multiplied by 100 divided by weight taken gives per cent telurium.

[1] A. W. Peirce, Am. Jour. Sci. (4), 1416. Gooch, "Methods of Chemical Analysis," 376.

[2] Cautious heating is necessary to prevent mechanical loss of tellurium during the volatilization of selenium.

Determination as Tellurium Dioxide

The following procedure worked out by Browning and Flint [1] provides for the direct estimation of tellurium in the form of its dioxide, TeO_2, in presence of selenium. The oxide is not affected by the air, it is anhydrous, non-hydroscopic and may be obtained in pure form. Selenium and tellurium are precipitated by sulphur dioxide from a hydrochloric acid solution according to the procedures given. The elements are filtered off, dissolved in hydrochloric acid containing sufficient nitric acid to cause solution and carefully taken to dryness on the water bath. The mixture is then treated as follows:

Procedure. The material is dissolved in hydrochloric acid, or in a 10% solution of potassium hydroxide, using about 2 cc. per 0.2 gram of dioxide. The solution, if alkaline, is slightly acidified with hydrochloric acid and then diluted to 200 cc. with boiling water. Dilute ammonium hydroxide is now added in faint excess, followed by the faintest possible excess of acetic acid, whereby the finely crystalline tellurium dioxide is precipitated. The precipitate is transferred to the perforated crucible containing an asbestos mat, and washed rapidly with cold water, then dried to constant weight at 105° C. and weighed as TeO_2.

NOTES. The addition of a few drops of acetic acid, as recommended, causes the precipitation to become quantitative when the solution has cooled.

Hot water is used for the dilution, since cold water induces a flocky precipitation with inclusion of selenious acid.

VOLUMETRIC DETERMINATION OF SELENIUM AND TELLURIUM

Iodometric Determination of Selenic, or Telluric Acid—Reduction with Hydrochloric Acid and Distillation

The method depends upon the reduction of selenic or telluric acid to selenious or tellurious acid by heating with hydrochloric acid, the evolved chlorine being a measure of the acids in question. The chlorine absorbed in potassium iodide solution liberates its equivalent of iodine, which may readily be determined by titration with standard thiosulphate. The following reactions illustrate the change that takes place:

$$K_2SeO_4 + 4HCl = 2KCl + H_2SeO_3 + H_2O + Cl_2,$$
$$K_2TeO_4 + 4HCl = 2KCl + H_2TeO_3 + H_2O + Cl_2,$$

$1\ Cl. = 1\ I = \frac{Se}{2}$ or $\frac{Te}{2} = 63.75$ grams Te or 39.6 grams Se per liter normal solution.

According to Gooch and Evans [2] over 30% of strong hydrochloric acid (sp.gr. 1.20) should be present. Dilute hydrochloric acid having a strength of 10% of HCl, sp.gr. 1.2, does not react with liberation of chlorine. Care must be taken not to prolong the boiling after the solution reaches a concentration of half strength, since over reduction may take place and the metals be liberated.

[1] Philip E. Browning and Wm. R. Flint, Am. Jour. Sci. (4), 28, 112. F. A. Gooch, "Methods in Chemical Analysis," John Wiley & Sons, Pub.

[2] F. A. Gooch and P. S. Evans, Jr., Am. Jour. Sci., (3), 1, 400.

Procedure. The sample containing the selenate or tellurate is treated with 75 cc. of hydrochloric acid, containing 25 cc. of strong HCl, sp.gr. 1.20, per 0.2 gram of the oxides, in a distillation flask connected with a Drexel wash bottle receiver, water cooled, and charged with potassium iodide solution. A current of CO_2 is passed into the flask to sweep the liberated chlorine into the iodide solution. The sample is boiled until nearly one-third its volume has distilled into the receiver. The liberated iodine is titrated with standard thiosulphate. One cc. N/10 $Na_2S_2O_3$ = 0.00396 gram Se or 0.006375 gram Te.

SILICON

WILFRED W. SCOTT

Si, *at. wt.* 28.3; *sp.gr. amor.* 2.00.; *crys.* 2.49; *m.p.* 1420° C.; *oxides* SiO,[1] SiO_2

DETECTION

The finely ground sample together with a small quantity of powdered calcium fluoride is placed in a small lead cup 1 cm. in diameter and depth (see Fig. 58), and a few drops of concentrated sulphuric acid added. A lead cover, with a small aperture, is placed on the cup, and the opening covered with a piece of moistened black filter paper. Upon this paper is placed a moistened pad of ordinary filter paper. The cup is now gently heated on the steam bath. At the end of about ten minutes a white deposit will be found on the under side of the black paper, at the opening in the cover, if an appreciable amount of silica is present in the material tested.[2]

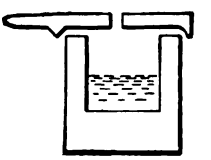


FIG. 58.

A silicate, fused with sodium carbonate or bicarbonate in a platinum dish and the carbonate decomposed by addition of hydrochloric acid with subsequent evaporation to dryness, will liberate silicon as silicic anhydride, SiO_2. The silica placed in a platinum dish is volatilized by addition of hydrofluoric acid, the gaseous silicon fluoride being formed. A drop of water placed in a platinum loop, held in the fumes of SiF_4, will become cloudy owing to the formation of gelatinous silicic acid and fluosilicic acid,

$$3SiF_4+3H_2O=H_2SiO_3+2H_2SiF_6.$$

If a silicate is fused in a platinum loop with microcosmic salt, the silica floats around in the bead, producing an opaque bead with weblike structure upon cooling.

ESTIMATION

The gravimetric procedure is the only satisfactory method for the estimation of silica. The substance in which the element is combined as an oxide or as a silicate is decomposed by acid treatment or by fusion with an alkali carbonate or bicarbonate, the material taken to dryness with addition of hydrochloric acid, whereby the compound silica is liberated. If other elements are present the silica is volatilized by addition of hydrofluoric acid and estimated by the loss of weight of the residue.

The element silicon has no important application. Its use for electrical resistance has been suggested. A rod 10 cm. long with cross section of 40 sq.mm. has a resistance of 200 ohms against a carbon rod of the same dimensions of 0.15

[1] Dictionary of Applied Chemistry. Thorpe, page 671.
[2] Philip E. Browning, Am. Jour. Sci. (4), **32**, 249.

ohm. Impure silica finds use in fluxes in manufacture of glass; pure silica for the manufacture of silica ware. With caustic it forms an adherent sodium silicate. Silicon carbide, carborundum, is used for refractory purposes, fire brick, zinc muffles, coke ovens. Crystolon, the crystalline form, is used as an abrasive, in making grinding wheels, sharpening stones, etc.

Combined as SiO_2 and in silicates the element is very widely distributed in nature and is a required constituent in practically every complete analysis of ores, minerals, soils, etc. It is present in certain alloys, ferro-silicon, silicon carbide, etc.

The element is scarcely attacked by single acids, but is acted upon by nitric-hydrofluoric acid mixture. It dissolves in strong alkali solutions. Silica is decomposed by hydrofluoric acid and by fusion with the fixed alkali carbonates or hydroxides.

Preparation and Solution of the Sample

General Considerations. The natural and artificially prepared silicates may be grouped under two classes: 1. Those which are decomposed by acids. 2. Silicates not decomposed by acids. The minerals datolite, natrolite, olivine and many basic slags are representative of the first class, and feldspar, orthoclase, pumice and serpentine are representative of silicates not decomposed by acids. (See more complete list under List of More Important Silicates, page 369.) The first division simply require an acid treatment to isolate the silica, the latter class require fusion with a suitable flux.

In technical analysis, in cases where great accuracy is not required, the residue remaining, after certain conventional treatments with acids, is classed as silica. This may consist of fairly pure silica or a mixture of silica, undecomposed silicates, barium sulphate and certain acid insoluble compounds. For accurate analyses this insoluble residue is not accepted as pure silica, unless impurities, which are apt to be found with the silica residue, are known to be absent from the material under examination.

Although the procedure for isolation of silica is comparatively simple, errors may arise from the following causes:

1. Imperfect decomposition of the silicate.
2. Loss of the silica by spurting when acid is added to the carbonate fusion.
3. Slight solubility of silica, even after dehydration, especially in presence of sodium chloride and magnesia.
4. Loss due to imperfect transfer of the residue to the filter paper.
5. Mechanical loss during ignition of the filter and during the blasting, due to the draft whirling out the fine, light silica powder from the crucible.
6. Error due to additional silica from contaminated reagents or from the porcelain dishes or glassware in which the solution was evaporated. A blank of 0.01% on the sodium carbonate will make an error of 0.1% per gram sample in an ordinary fusion where 10 grams of the flux are required.
7. Error due to loss of weight of the platinum crucible during the blasting.
8. Incomplete removal of water, which is held tenaciously by the silica. Furthermore, weighing of the residue should be done quickly, as the finely divided silica tends to absorb moisture.

Two general procedures will be given for treatment of the acid decomposable and undecomposable silicates. It is frequently advisable to use these two procedures in conjunction, extracting the material first with acid, and then fusing

ıe insoluble residue with sodium carbonate; this procedure is used when a ritty residue remains after the acid extraction. Following the general procedures ɔr decomposition of silicates, certain special methods will be given.

List of Most Important Silicates. Silicates decomposed by acids. Allanite; allo-ɔhane; analcite; botryolite; brewsterite; calamine; chabasite; croustedtitite; datolite hydrated silicate and borate of Ca with Al and Mg); dioptase; eulytite; gadolin-te; gahlenite; helvite; ilvaite (silicate ferrous and ferric iron with Al_2O_3, CaO and MgO); laumonite; melinite; natrolite (hydrated silicate of Al and Na with Fe and Ca()); okenite; olivine (silicate of Fe and Mg); pectolite; prehenite (hydrated Al and Ca silicate with Fe, Mn, K, Na, etc.); teproite; wernerite; woolastonite; zaolite.

Silicates undecomposed by acids. Albite; audalusite; augite; axinite; beryl; carpholite; cyanite; diallage, epidote (silicate of Fe, Al and Ca with FeO, Mn, Mg, K, Na); euclase; feldpsar (silicate of K, Na, Al, Fe, Ca and Mg); garnet; iolite; labradorite; (micas of K and Mg); orthoclase; petalite; pinite, prochlorite; pumice; serpentine; sillimanite, talc, topaz, tourmaline (Fe_2O_3, FeO, Mn, Al, Ca, Mg, K, Na, Li, SiO_2, B_2O_3, P_2O_5, F); vesuvianite.

Preparation of the Substance for Decomposition

If the material is an ore or mineral it is placed on a steel plate within a steel ring and broken down by means of a hardened hammer to small lumps and finally to a coarse powder. A quartered portion of this is air dried and ground as fine as possible in an agate mortar and preserved in a glass-stoppered bottle for analysis.

Analyses are based on this air-dried sample. If moisture is desired it may be determined on a large sample of the original material. Hygroscopic moisture is determined on the ground, air-dried sample, by heating for an hour at 105 to 107° C.

Decomposition of the Material, General Procedures

Silicates Decomposed by Acids

Acid extraction of the silicates. 0.5 to 1 gram of the finely pulverized material placed in a beaker or casserole is treated with 10 to 15 cc. of water and stirred thoroughly to wet the powder.[1] It is now treated with 50 to 100 cc. of strong hydrochloric acid and digested on the water bath for fifteen or twenty minutes with the beaker or casserole covered by a watch-glass. If there is evidence of sulphides (pyrites), etc., 10 to 15 cc. of concentrated nitric acid are now added and the containing vessel again covered. After the reaction has subsided, the glass cover is raised by means of riders and the mixture evaporated to dryness on the water bath. (This evaporation may be hastened by using a sand bath, boiling down to small bulk at comparatively high temperature, then to dryness on the water bath. Decomposition is complete if no gritty particles remain. A flocculent residue will often separate out during the digestion, due to partially dehydrated silicic acid, hydrated silicic acid, $Si(OH)_4$ is held in solution.) The silicic acid is converted to silica, SiO_2, the residue taken up with dilute hydrochloric acid, silica filtered off, washed with water acidified with hydrochloric acid, and estimated according to the procedure given later.

[1] Water is added to the sample and then acid, as strong acid added directly would cause partial separation of gelatinous silicic acid, which would form a covering on the undecomposed particles, protecting them from the action of the acid.

Silicates Not Decomposed by Acids

Fusion with Sodium Carbonate or Sodium Bicarbonate. 0.5 to 1 gram of the air-dried, pulverized sample is placed in a large platinum crucible or dish in which has been placed about 5 grams of anhydrous sodium carbonate. The sample is thoroughly mixed with the carbonate by stirring with a dry glass rod, from which the adhering particles are brushed into the crucible. A little carbonate is sprinkled on the top of the mixture and the receptacle covered. It is heated to dull redness for five minutes and then gradually heated up to the full capacity of a Méker burner. When the mix has melted to a quite clear liquid, which generally is accomplished with twenty minutes of strong heating, a platinum wire with a coil on the immersed end is inserted in the molten mass, and this allowed to cool. The fusion is removed by gently heating the crucible until the outside of the mass has melted, when the charge is lifted out on the wire, and after cooling disintegrated by placing it in a beaker containing about 75 cc. dilute HCl (1 part HCl to 2 parts H_2O), covering the beaker to prevent loss by spattering. The crucible and lid are cleaned with dilute hydrochloric acid, adding this acid to the main solution. When the disintegration is complete, the solution is evaporated to dryness and silica is estimated according to directions given later.

If decomposition is incomplete, gritty material will be found in the beaker upon treatment of the fusion with dilute acid. If this is the case, it should be filtered off and fused with a second portion of sodium carbonate, and the fusion treated as directed above.

NOTES. Fusions with soluble carbonates are generally best effected with the sodium salt, except in fusions of niobates, tantalates, tungstates, where the potassium salt is preferred on account of the greater solubility of the potassium compounds. Sodium alone has an advantage over the mixed carbonates, $Na_2CO_3+K_2CO_3$, as silica has a high melting-point and a flux, which fuses at 810° C., is more apt to cause disintegration of the silicate than the mixture, which melts at 690° C.

Prolonged blasting is undesirable, as it renders the fusion less soluble. Aluminum and iron are also rendered difficultly soluble, when their oxides are heated to a high temperature for some time.

If the melt is green, it is best to dissolve out the adhering melt from the crucible with dilute nitric acid, as a manganate (indicated by the color), if present, will evolve free chlorine by its action on HCl and this would attack the platinum.

Fluorides.[1] In presence of fluorides the melt is extracted with water (an acid extraction would volatilize some of the silica), and the extract filtered off from the insoluble carbonates. To the filtrate is added about 5 grams of solid ammonium carbonate, and the mix warmed to 40° C. and allowed to stand for several hours. The greater part of the silica is precipitated. This is filtered off and washed with water containing ammonium carbonate. Preserve this with the insoluble carbonate for later treatment. The filtrate, containing small amounts of silicic acid, is treated with 1 to 2 cc. of ammoniacal zinc oxide solution (made by dissolving C.P. moist zinc oxide in ammonia water). The mixture is boiled to expel ammonia and the precipitate of zinc silicate filtered off. The precipitate is washed into a beaker through a hole made in the filter, and the adhering material dissolved off with dilute HCl, enough being added to dissolve the remaining residue. This is evaporated to dryness and silica separated as usual. Meantime the insoluble carbonate is dissolved with HCl, evaporated to

[1] Sodium bicarbonate may be used in place of the carbonate with excellent results.

ness and any silica it contains recovered. Finally all three portions of ica are combined, ignited and silica estimated as usual.

Special Procedures for Decomposing the Sample

Treatment of Iron and Steel for Silica. One gram of pig-iron castings, 5 grams of steel are taken for analysis, both the fine and coarse drillings being ken in about equal proportion. (Fine particles contain more silicon than e coarse chips.) Twenty to 50 cc. of dilute nitric acid (sp.gr. 1.135) are added the sample in a 250-cc. beaker or small casserole, and this covered. If the tion is violent, cooling, by placing the beaker in cold water until the violent tion has subsided, is advisable. Twenty cc. of 50% sulphuric acid are added d the solution evaporated on the hot plate to SO_3 fumes. After cooling, 50 cc. of water are added and 2 to 5 cc. dilute sulphuric acid. The mixture is ated until the iron completely dissolves and the silica is filtered off onto an hless filter, washed with hot dilute hydrochloric acid (sp.gr. 1.1), and with ot water until free from iron. The residue is ignited and the silica estimated according to the procedure given later.

Pig iron and cast iron may be decomposed by digestion with a mixture of 8 parts by volume of HNO_3 (sp.gr. 1.42), 5 parts of H_2SO_4 (sp.gr. 1.84), and 17 parts of water.

Steel and wrought iron may be disintegrated by a mixture of 8 parts by volume of HNO_3 (sp.gr. 1.42), 4 parts H_2SO_4 (1.84), and 15 volumes of water.

Ferro Silicons. Dilute hydrochloric acid, 1 volume of acid (sp.gr. 1.19), with 2 volumes of water is a better solvent than the strong acid.

Steels Containing Tungsten, Chromium, Vanadium and Molybdenum. Fusion with potassium acid sulphate, $KHSO_4$, in a platinum dish, or sodium peroxide in a nickel crucible will generally decompose the material. Sodium peroxide is of special value in decomposing chromium alloys.

Silicon Carbide, Carborundum. This is best brought into solution by fusion with potassium hydroxide in a nickel crucible. Sulphuric, hydrochloric, nitric acids, or aqua regia have no effect upon this refractory material.

Sulphides, Iron Pyrites, etc. These require oxidation with strong nitric acid or a mixture of bromine and carbon tetrachloride, followed by nitric, exactly according to the procedure given for solution of pyrites in the determination of sulphur. The sample is taken to dryness and then hydrochloric acid added and the solution again evaporated. The residue is dehydrated and silica determined as usual.

Slags and Roasted Ores. Digestion with hydrochloric acid according to the first general procedure is best. The addition of nitric acid to decompose sulphides may be necessary.

Decomposition of silicates by fusion with lead oxide (method of Jannasch), and calcium carbonate and ammonium chloride (method of Hillebrand), are of value when sodium is desired on the same sample. The procedures are given under chapters on Sodium and Potassium.

NOTE. K_2CO_3 is preferred to Na_2CO_3 for fusion of tungstates, niobates and tantalates on account of the greater solubility of the potassium salts. For corundum and alumina silicates Na_2CO_3 is preferred as double salt of potassium and aluminum are less soluble than the sodium salt.[1]

Fluorides of silicon are fused with boric acid, BF_3 is volatilized, SiF_4 is not formed. P. Jannasch.[2]

[1] J. L. Smith, Am. Jour. Sci. (2), **40**, 248, 1865. C. N., **12**, 220, 1865.
[2] Ber., **28**, 2822, 1896.

PROCEDURE FOR THE DETERMINATION OF SILICON AND SILICA

As has been stated, the gravimetric method for determination of silica is the only satisfactory procedure for estimation of this substance. The oxidation of the element and its isolation have been dealt with in the section Preparation and Solution of the Sample. The following directions are for purification and final weighing of the element in the form of its oxide, silica, SiO_2.

Extraction of the Residue—First Evaporation. The residue, obtained by evaporation of the material after decomposition of the silicate, by acids or by fusion, as the case required, is treated with 15–25 cc. of hydrochloric acid (sp.gr. 1.1) covered and heated on the water bath 10 minutes. After diluting with an equal volume of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. hydrochloric acid (sp.gr. 1.2) to 95 cc. of water. This filtration may be performed with suction, and then with hot water. The filtrate and washings are evaporated to small volume on a sand bath and finally to dryness. This contains the silica that dissolved in the first extraction.

Second Evaporation. The residue obtained from evaporation of the filtrate is dehydrated for 2 hours at 105–110° C.[1] and extracted with 10 cc. of hydrochloric acid (sp.gr. 1.1) covered and heated on the water bath for ten minutes diluted to 50 cc. with cold water and filtered immediately, without suction. The residue is washed with cold water containing 1 cc. concentrated hydrochloric acid to 99 cc. water, the washed residue containing practically all[2] the silica, that went into solution in the first extraction, is combined with the main silica residue. This is gently heated in a platinum crucible until the filters are thoroughly charred, and then ignited more strongly to destroy the filter carbon and finally blasted over a Méker burner for at least thirty minutes, or to constant weight, the crucible being covered. After cooling the silica is weighed. For many practical purposes this residue is accepted as silica, unless it is highly colored. For more accurate work, especially where contamination is suspected (silica should be white), this residue is treated further.

Estimation of True Silica. Silica may be contaminated with $BaSO_4$, TiO_2, Al_2O_3, Fe_2O_3, P_2O_5 combined (traces of certain rare elements may be present). The weighed residue is treated with 3 cc. of water and 5 cc. of hydrofluoric acid, HF (hood), followed by several drops of concentrated sulphuric acid. After evaporation to dryness, the crucible is heated to redness and again cooled and weighed. The loss of weight represents silica, SiO_2.[3]

[1] Dehydration of silica is aided by the presence of lime and retarded by magnesia. In presence of the latter a soluble magnesium silicate will form if the dehydration is conducted at a temperature much above 110° C., hence it is better to avoid this by taking more time and heating to 100 or 105° as recommended.

Sodium chloride has a solvent action on silica, the reaction of HCl on sodium silicate being reversible; $2HCl + Na_2SiO_3 \leftrightarrows 2NaCl + H_2SiO_3$. An evaporation of the filtrate to dryness will recover the greater part of the silica thus dissolved.

[2] Not more than 0.1% of the original SiO_2 may still be in solution.

[3] Silicic acid cannot be completely dehydrated by a single evaporation and heating, nor by several such treatments, unless an intermediate filtration of silica is made. If, however, silica is removed and the filtrate again evaporated to dryness and the residue heated, the amount of silica remaining in the acid extract is negligible. (See Article by Dr. W. E. Hillebrand, Jour. Am. Soc., 24.)

NOTES. Lenher and Truog make the following observations for determining silica:[1]

1. In the sodium carbonate fusion method with silicates, there is always a non-volatile residue when the silica is volatilized with hydrofluoric and sulphuric acids.
2. The non-volatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.
3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110°.
4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible.
5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.
6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminum, which do not dissolve completely in hydrochloric acid.
7. Hydrochloric acid (sp.gr. 1.1) in minimum amount should be used first to wet the dehydrated chlorides and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off as quickly as possible.
8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then commonly hydroscopic.
9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.
10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the solutions which act as solvents.
11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.
12. Excessive time of dehydration, viz., four hours, possesses no advantages.
13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4–5 sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient completely to decompose many silicates.
14. The non-volatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no non-volatile residue.

ANALYSIS OF SILICATE OF SODA

Determination of Na_2O

Five grams of the sample are dissolved in about 150 cc. of water and heated; 1 cc. of phenolphthalein is added and then an excess of standard sulphuric acid from a burette. The excess acid is titrated with standard sodium hydroxide to a permanent pink.

$$H_2SO_4 \times 0.6321 = Na_2O.$$

Silica. Ten grams of the sample are acidified with hydrochloric acid and evaporated to dryness on the steam bath. The treatment is repeated with additional hydrochloric acid and then the residue taken up with 5 cc. of the acid and 200 cc. of water. The residue is digested to dissolve the soluble salts, filtered, washed and ignited. Silica is determined by loss of weight by volatilization of the silica with hydrofluoric and sulphuric acids. The filtrate is made to 1 liter.

Iron and Alumina. Five hundred cc. (5 grams) of the filtrate from the silica determination are oxidized with HNO_3 and the iron and alumina precipitated with ammonia, washed, ignited and weighed as Al_2O_3 and Fe_2O_3. The residue is dissolved by digestion with hydrochloric acid or by fusion with sodium acid

[1] Victor Lenher and Emil Truog, Jour. Am. Chem. Soc., 38, 1050, May, 1916.

sulphate, and subsequent solution in hydrochloric acid. Iron is determined by titration in a hot hydrochloric acid solution with standard stannous chloride, $SnCl_2$, solution as usual. If only a small amount of precipitate of iron and alumina is present, as is generally the case, solution by hydrochloric acid is preferable to the fusion with the acid sulphate. The latter is used with larger amounts of the oxides.

Lime, CaO. This is determined in the filtrate from iron and alumina by precipitation as the oxalate and ignition to CaO.

Magnesia, MgO. This is determined in the filtrate from lime by precipitation with sodium ammonium phosphate. The precipitate is ignited and weighed as $Mg_2P_2O_7$ and calculated to MgO. Precipitate $\times 0.3621 = MgO$.

Combined Sulphuric Acid. One hundred cc. of the filtrate from the silica determination (=1 gram) is treated with $BaCl_2$ solution and sulphuric acid precipitated as $BaSO_4$.

$$BaSO_4 \times 0.4202 = H_2SO_4 \quad \text{or} \quad \times 0.3430 = SO_3.$$

Sodium Chloride. Ten grams of the silicate of soda is dissolved in 100 cc. of water and made acid with HNO_3 in slight excess and then alkaline with MgO. Cl is titrated with standard $AgNO_3$ solution.

Water. This is determined either by difference or by taking 10 grams to dryness and then heating over a flame and blasting to constant weight.

NOTE. For detailed procedures for each of the above see special subject.

ANALYSIS OF SAND, COMMERCIAL VALUATION

Silica. Two grams of the finely ground material is fused in a platinum crucible with 10 grams of fusion mixture ($K_2CO_3 + Na_2CO_3$) by heating first over a low flame and gradually increasing the heat to the full blast of a Méker blast lamp. When the fusion has become clear it is cooled by pouring on a large platinum cover. The fused mass on the cover and that remaining in the platinum crucible are digested in a covered beaker with hot hydrochloric acid on the steam bath. The solution is now evaporated to dryness, taken up with a little water and 25 cc. of concentrated HCl and again taken to dryness. Silica is now determined by the procedure outlined under the general method on page 372.

Ferric Oxide and Alumina. The filtrate is oxidized with crystals of solid potassium chlorate, $KClO_3$, and iron and aluminum hydroxides precipitated with ammonia. The precipitate is filtered, washed, ignited and weighed as $Al_2O_3 + Fe_2O_3$.

Calcium Oxide. To the ammoniacal filtrate 10 cc. of ammonium oxalate solution are added, the solution heated to boiling and the precipitate allowed to settle until cold. The solution should not be over 200 cc. The calcium oxalate is filtered off, washed and ignited. The residue is weighed as CaO.

Magnesium Oxide. The filtrate from the lime is made strongly ammoniacal and 10 cc. of sodium ammonium phosphate added. The solution during the addition is allowed to stand cold for some time, three to four hours. The precipitate is filtered and washed with dilute ammonia (1 of reagent to 3 parts of water), then ignited and weighed as $Mg_2P_2O_7$. This weight multiplied by $0.3621 = MgO$.

For more detailed directions see the individual subjects under the chapters devoted to the element.

SILVER

W. G. DERBY

Ag, *at.wt.* 107.88; *sp. gr.* 10.50–10.57; *m.p.* 960.5° C.; *b.p. about* 1950° C.; *oxides*, Ag_2O, Ag_4O, Ag_2O_3

DETECTION

A trace of silver in most substances is detected with greatest certainty by furnace assay methods.

The wet method of detection of silver most commonly practiced, depends upon observation of the properties of the precipitate formed by the addition of a not excessive amount of alkaline chloride to a cold nitric or sulphuric acid solution of the substance undergoing examination. One-tenth milligram of silver precipitated as silver chloride in a cold 200-cc. acid solution gives a very perceptible opalescence to the liquid.

Silver chloride is white when freshly precipitated, tinted pink when palladium is present; in colorless liquids on exposure to light turns brown, violet, blue or black. By agitation, heating or long standing the precipitate becomes coagulated or granular and in such a state is retained by an ordinary filter. The presence of some forms of organic matter prevents coagulation.

Silver chloride is dissolved by concentrated hydrochloric acid; raising the temperature of the acid assists the action. It is dissolved by sodium thiosulphate, alkali cyanides, mercuric nitrate, and alkaline chlorides.

From mercurous chloride, silver chloride, except when constituting a small proportion of the precipitate, is distinguished by its solubility without decomposition in ammonia. Precipitation from its ammoniacal solution is accomplished by acidifying. Lead chloride, precipitable also by hydrochloric acid, is not flocculent, does not coagulate, but dissolves quite freely by heating. Addition of hydrochloric acid to a solution of silicon, tellurium, thallium, tungsten or molybdenum may produce a precipitate, in each case, easily distinguishable from that of silver chloride, but may mask traces of the salt.

Silver, in a cold solution containing free nitric acid, only a small amount of colored salts and no mercury, may be detected through the formation of a white precipitate, similar in appearance to silver chloride, by addition of a slight excess of an alkaline thiocyanate.

When a solution of silver salt [1] is added to a mixture of 20 cc. ammonium salicylate (20 grams. salicylic acid neutralized with ammonia, a slight excess added and the whole made up to 1000 cc.) and 20 cc. of a 5% solution of ammonium persulphate added, an intense brown color is produced, which will detect the presence of a 0.01 milligram of silver. Lead does not affect the test.

When it appears that the chloride or thiocyanate test for silver is not positive on account of the presence of other precipitable elements, the precipitate, after it

[1] A. W. Gregory, Chem. Soc. Proc., 24, 125, 1908.

settles, is filtered through the finest quality of paper, and the mixture of the ash of the incinerated filter with dry potassium carbonate heated on charcoal with a mouth blowpipe. If silver is present and not associated with a large amount of palladium, there will be found on the charcoal pellicles of the color characteristic of silver, which have no white or yellow sublimate when melted in the oxidizing flame of the blowpipe. The pink palladium salts of silver precipitated by a chloride or thiocyanate before the blowpipe produces metal which is dull in appearance and not readily melted.

NOTES. Silver may be recognized in a solution of concentration 1 to 240,000 by the reduction of its salts with alkaline formaldehyde.[1] Whitby's[2] method of detection and estimation of small amounts of silver depends upon the formation of a yellow color through addition of sucrose and sodium hydrate. Ammonium hydrate interferes, but bismuth, cadmium, copper, mercury of either valence, lead or zinc, in amounts equal to that of the silver, do not.[3] Maletesta and DeNola add to the solution to be tested a few drops of a solution of nitrate of chromium and then potassium hydrate to alkalinity. A brownish turbidity or black precipitate of silver oxide forms. The limit of sensitiveness is 0.5 milligram in 100 cc.

ESTIMATION

Silver is determined in copper, lead, silver, sulphur or other ores, in copper and lead furnace by-products, and in lead by furnace assay methods, in which a preliminary acid treatment of the sample is rarely employed; in native copper ore, in copper, copper alloys, gold, gold alloys and in the slime from the electrolytic refining of copper or lead by furnace methods, in which a preliminary acid treatment of the sample is employed, in silver alloys by volumetric or gravimetric methods; in mercury by a gravimetric method; in cyanide mill solution or solutions containing much organic matter by furnace process on the residue obtained by evaporation or precipitation; in silver plating electrolyte by electrolysis.

Solubility. Nitric acid, dilute or concentrated, attacks silver rapidly when hot. The presence of a soluble chloride, iodide or bromide in the solvent or substance will retard and may prevent solution. Unless oxidizing agents are present, dilute sulphuric acid has practically no action on massive silver, but hot, strong acid commences to be an active solvent at a concentration of 75% H_2SO_4. Hydrochloric acid attacks silver superficially. The action of alkaline hydrates or carbonates in solution is inappreciable; in a state of fusion, slight.

Furnace Assay Methods. These will be described in the chapter devoted to that subject.

GRAVIMETRIC METHODS

Determination as Silver Chloride

The method is not of extreme accuracy in the presence of much antimony, mercury or lead. By precipitating silver chloride in a well-diluted solution by a weak solution of the precipitant, the error, on account of its property of tenaciously retaining salts, may be made very small. Because of its tendency to decompose, the precipitate of silver chloride should not be exposed to direct sunlight or allowed to stand for many hours.

[1] Armani and Barboni, Zeit. Chem. Ind. Kolloide, **6**, 290.
[2] Zeit. Anorg. Chem., **67**, 62; C.A., **4**, 1444.
[3] Bull. Chim. Farm., **52**, 533.

To the hot nitric or sulphuric acid solution of silver, diluted to about 500 cc., is added, with constant stirring, a few cc. at a time, and to only slight excess, a solution of hydrochloric acid containing $\frac{1}{10}$ the per cent HCl.

The precipitate of silver chloride is coagulated by heating, or brisk stirring, the liquid cooled to room temperature and filtered through a tared Gooch crucible, which has been thickly bottomed with fiber asbestos. The precipitate is washed with water containing a little nitric acid. The dried crucible is heated over a flame until the edges of the precipitate begin to fuse.

$$AgCl \times 0.7526 = Ag.$$

NOTE. Alifeld [1] adds 5 cc. ether to the halide solution, before precipitation, to hasten coagulation.

Determination as Silver Cyanide

In the analysis of mercury, the nitric acid solution of the metal is nearly neutralized with a solution of sodium carbonate. Potassium cyanide solution is then added until the precipitate, which first forms, is dissolved. Then under a hood with strong draft, dilute nitric acid is added in slight excess of the quantity required to combine with the base in the amount of potassium cyanide present. The precipitate of silver cyanide, practically insoluble in dilute nitric or hydrocyanic acid, is coagulated by stirring or long standing and filtered from the cold solution of mercuric nitrate by use of a tared paper-bottomed Gooch crucible. The precipitate is washed with cold dilute nitric acid (1–10) until a test of the washings with hydrogen sulphide shows the absence of mercury. The crucible is dried at 212° to constant weight.

$$AgCN \times 0.8057 = Ag.$$

NOTES. Determination of silver as metal through precipitation with hypophosphorous acid [2] as silver sulphide or as silver chromate [3] are methods of doubtful technical application.

Electrolytic Method [4]

According to the strength of the silver bath 10 or 20 cc. are filtered into a tared 200-cc. platinum dish and according to the greater or smaller excess of cyanide present, $\frac{1}{2}$ to 1 gram of potassium cyanide in solution is added. The electrolyte diluted to about a half inch from the edge of the dish is kept, by a flame underneath, at a temperature of 140 to 149° F. during the period of electrolysis at $N.D._{100} = 0.08$ amp.

Complete precipitation, which requires three to three and a half hours, is recognized by test with ammonium sulphide. Without interruption of the current, by use of a siphon, displacement of the electrolyte with water is accomplished. The dish is rinsed with alcohol and ether, dried at 212°, weighed and silver obtained calculated to grams per liter or cubic foot.

NOTES. Benner and Ross [5] deposit 0.15 gram in twenty minutes with a current of 3 amperes from 50 cc. of electrolyte containing 8 grams potassium cyanide and 2 grams potassium hydrate on a 9-gram platinum gauze cathode.

[1] Z. anal. Chem., 48, 79.
[2] Mawrow and Mollow, Zeit anorg. Chem., 61, 96.
[3] Gooch and Bosworth, Am. J. Sci., 27, 241.
[4] Langbein, "Electro-Deposition of Metals," 6th Ed.
[5] J. A. C. S., July, 1911, 1106.

Exner [1] using a platinum dish as the cathode and a 2-in. diameter bowl-shaped spiral anode revolving 700 R.P.M., deposited 0.4900 gram from about 125 cc. of a hot electrolyte containing 2 grams potassium cyanide in ten minutes at $N.D._{100}$ 2 amps.

The above methods presume the absence of other metals precipitable under the conditions mentioned.

VOLUMETRIC METHODS

Volhard's Thiocyanate Method. This method is especially adapted to determination of moderate quantities of silver in cold dilute nitric acid solutions which contain no mercury, nitrous acid, or a greater amount of yellow, red or brown-colored salts than will give an appreciable tint to the solution, and not so large amount of blue salts as will mask the end-point.

The presence of palladium and silver chloride interfere with the accuracy of the detemination. Bromide or iodide of silver [2] may be present.

The method is based on the greater affinity of silver than ferric for thiocyanate ions. When silver thiocyanate has been completely precipitated, the excess of alkali thiocyanate, in the presence of free nitric acid, reacts with a ferric salt with formation of a reddish-brown solution of ferric thiocyanate.

The ferric indicator may be made from ferric ammonium sulphate, ferric nitrate or from ferrous sulphate by adding a large excess of nitric acid to its concentrated solution and boiling to decompose nitrous acid. Whatever salt is used for indicator it should be free of chlorine, its solution made of constant ferric strength and used in quantities graduated according to the volume of the liquid titrated. A saturated solution of ferric ammonium sulphate (1 cc. to each 20 cc. of the liquid to be titrated), is a convenient form of indicator. The standard solution commonly employed for the determination of silver in silver plate, for the trial assay of Doré metal and for the assay of silver bullion by the Gay-Lussac pipette method has a silver value of 10 milligrams per cc. Since both the commonly employed thiocyanate salts are deliquescent, it is unnecessary to weigh out the exact quantity. Ammonium is less likely to contain chlorine than potassium thiocyanate. In the decimal solution (silver value 1 milligram per cc.), the liter content is 0.7–0.8 gram of ammonium or 0.9–1.0 gram of potassium thiocyanate. Solution is made with chlorine-free water.

For standardizing the decimal solution, 1 gram of standard silver is dissolved in a funnel-closed liter flask by 20 cc. of equal volumes of nitric acid and water. After boiling to decompose nitrous acid the solution is made up to mark with water at room temperature.

When using the standard thiocyanate solution with the object of obtaining very accurate results, it is good practice, instead of using a standard solution of silver, to obtain the standard by titrating, simultaneously with the assays, solutions of known quantities of standard silver approximately equal in amount and dissolved in the same manner as the assays.

In the operation of titration, after addition of the prescribed proportion of ferric indicator, standard thiocyanate solution is added from a burette to the cold silver solution in 500-cc. Erlenmeyer flask, until the rate of bleaching of the reddish-brown color slackens; then cautiously, with vigorous agitation after each addition,

[1] J. A. C. S., Sept., 1903, 900.
[2] Rosanoff and Hill, J. A. C. S., March, 1907, 273.

until the liquid shows a tendency to become clear above the settled precipitate and a reddish tint persists. The end-point tint obtained in standardizing the thiocyanate should be matched in titrating the assay solutions. In case the end-point is overrun, standard silver solution may be added until the correct tint is obtained, allowance being made for silver so added.

Since the shade of color at the end-point is dependent upon the concentration of ferric salt and inasmuch as volume, temperature, amount of free nitric acid and amount of silver present are conditions which have more or less influence upon the determination, such conditions as prevailed during the standardization of the thiocyanate solution should be maintained in the operation of the assay.

NOTES. Separation from colored salts may be brought about by precipitating the silver with a very slight excess of thiocyanate, allowing the precipitate to settle until the residual liquor is clear, washing by decantation through an alundum filter cone or asbestos-bottomed Gooch crucible, placing the filter and contents in the flask in which precipitation took place, adding strong nitric acid and heating until all silver thiocyanate is decomposed. Titration is made on the cold dilute solution.

Palladium, in quantity sufficient to color the solution, can be eliminated by removal of free acid through evaporation just to dryness, immediately taking up with water and adding a drop or two of a saturated solution of sodium acetate, (free of chlorine). Pure carbon monoxide is passed until the hot liquid is decolorized. The filtrate from the palladium after addition of an excess of nitric acid is titrated when cold.

When part of the silver is present as silver chloride, as an unavoidable product of the analysis, it should be removed by filtration and reduced on the filter with zinc dust after removal of the filtrate. The reduced silver is washed free of chloride, dissolved with hot 20% nitric acid, the solution washed from the filter, concentrated by boiling and added to the filtrate from the silver chloride. Titration may then be made on the silver solution.

In the application of the Volhard method to the assay of a cyanide mill solution,[1] a measured volume of the solution is run through a $\frac{1}{8}$-in. layer of zinc dust in a Gooch crucible with care to keep the zinc always covered with the solution. The zinc washed into beaker, is cautiously dissolved with nitric acid, the solution boiled, diluted and, when cold, titrated with a thiocyanate solution which has been standardized by a silver solution which contains an amount of zinc the same as used in the process of reduction.

Gay-Lussac Method

This very accurate method is especially adapted to the valuation of silver bullion, but may be applied in principle to the determination of silver in a nitric acid solution which contains as little as 100 milligrams of the metal, providing the volume of the solution is not so large or color so deep as to make a precipitate of silver chloride equivalent to 0.1 milligrams of silver indistinguishable. Metals whose presence interfere are mercury and tin.

The method is founded upon the almost absolute insolubility of silver chloride or bromide in cold dilute nitric acid and the property of the precipitate becoming so completely coagulated through agitation that it settles speedily, leaving a

[1] Clevenger, Eng. and Min. J., 95, 892, 1913.

liquid sufficiently clear to permit of observance of any precipitate produced by further addition of precipitant.

The presence of free sulphuric acid is prejudicial to a very close determination, because of the volume of liquid required to keep silver sulphate in solution, and also because the result of agitation after addition of precipitant, is apt to be a fine precipitate which does not readily settle.

The use of a bromide is preferable to a chloride salt as a reagent, because its silver salt is less affected by light, coagulates and settles more readily, will suffer more agitation before formation of a fine, slowly settling precipitate, but chiefly because on account of the greater insolubility of silver bromide, the end-point of the operation of titration is more sharply defined.

The reagents required consist of chlorine-free nitric acid, as standard solution of an alkali bromide or chloride of approximately decinormal strength, a decimal solution of the same salt having a silver-precipitating value of 1 milligram per cc., and a decimal silver solution containing 1 milligram of silver per cc. in the form of silver nitrate.

In the assay of silver bullion, the standard solution may contain 5.42 grams of sodium chloride or 11.03 grams of potassium bromide or 9.54 grams of dry sodium bromide per liter, and should have a silver precipitating value, as indicated by the method, of about 1 gram per 100 cc.

The factor of volume change per degree change of temperature from 15 to 21° C. is approximately 0.00012; from 20 to 26°, 0.00019; from 25 to 31° C., 0.00024.

Although the approximate precipitating value should be known by previous test, it is the better practice to determine the exact value by running two or more checks of pure silver simultaneously with each batch of assays than to apply the temperature correction factor.

The decimal salt solution is best made from C.P. salts, either 0.5149 gram sodium chloride or 1.1033 grams potassium bromide per liter.

The decimal silver solution is made by dissolving 1 gram of pure silver with a few cc. of nitric acid and making up to 1 liter with distilled water. (See Method for Preparation of Pure Silver, page 384.)

The apparatus required consists of a pipette which will deliver approximately 100 cc. with an accuracy of not over 5 milligrams variation in weight of the standard solution at constant temperature between successive deliveries, 10-cc. burettes with glass stopcocks; and 8-oz. narrow mouth, round, flint-glass bottles with high, tightly fitting stoppers; the assay bottles should be of a quality which will endure heating in a steam bath or in a hot plate.

The Stas or Ricketts overflow pipette, listed by all laboratory supply firms, is the type most commonly used. This pipette is filled by gravity flow through a rubber tube from the standard solution reservoir connected to the discharge-end. When the liquid overflows, the top is closed by finger, the pinchcock closed, the supply tube removed and the hanging drop wiped off.

Care to avoid introduction of air bubbles into the pipette, uniform habit in respect to pressure of the finger on the top, and method of wiping off the hanging drop, must be practiced to obtain good results.

The automatic dividing pipette with three-way stopcock shown in the illustration, will give remarkably accurate deliveries when properly constructed and manipulated. This type of pipette of the form ordinarily furnished by supply houses, will rarely deliver with sufficient accuracy for bullion assays.

Since the end-point by the Gay-Lussac method depends upon the observance

of cessation of precipitation, it is evident, in order to avoid undue tediousness in its operation, that the silver content of the amount of sample taken for assay should be known within a few milligrams.

This may be ascertained by assay of 1 gram of the sample by the Volhard method, using a thiocyanate solution of decinormal strength, or by cupellation with application of a correction for cupel absorption.

The approximate silver value having been determined, such an amount of the sample is weighed out and placed in an assay bottle, as will contain silver in slight excess of the silver equivalent of the pipette full of standard salt solution. Ten to 15 cc. of nitric (1.26 sp.gr.) acid are added and the bottle kept in a steam bath or on a moderately hot plate until solution of silver is complete.

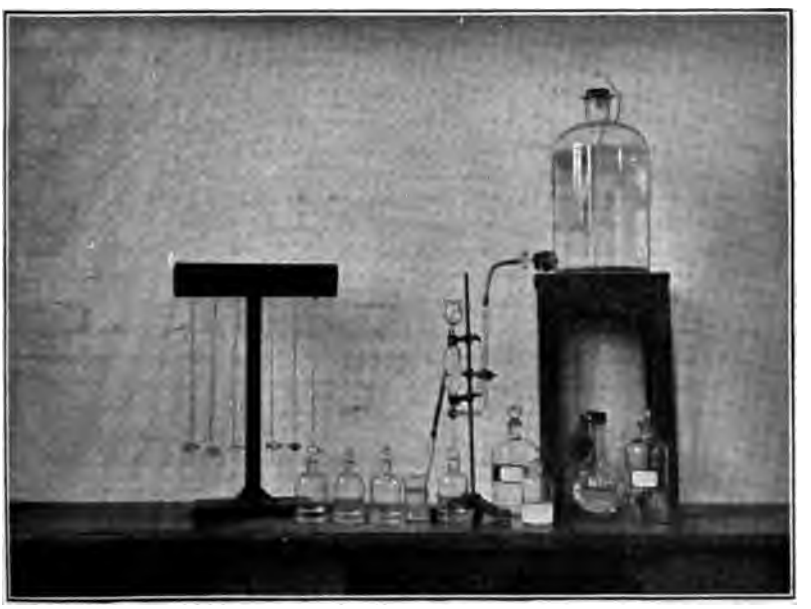


FIG. 59.—Apparatus for Determining Silver. Gay-Lussac Method.

To the cold solution of the sample is added a pipette full of the standard salt solution and the tightly stoppered bottle agitated until the precipitate will settle with sufficient completeness to permit of observance of any turbidity produced by addition of either of the decimal solutions.

More agitation than is absolutely necessary should be avoided, because of the increasing tendency of the precipitate toward the fine granular form, which settles slowly.

On account of alteration of the character of the precipitate by sunlight, the titration should be carried out in a shaded place and as expeditiously as possible.

One-tenth cc. of the decimal salt solution is dropped into the bottle, and holding the bottle against a dark background, the appearance of the cloud of precipitate is noted

From the character of the precipitate, after some practice, it is possible to judge whether a single cc. or more may be added at once, or whether the titration must be continued by one-tenth cc. additions.

Until the non-appearance of cloudiness indicates the end-point, the bottle should be agitated after each addition of decimal salt solution.

If the pipette full of standard solution is more than sufficient to precipitate the silver, or in case the end-point has been run over, decimal silver solution is added in 1 cc. portions until precipitation ceases. Decimal salt solution is then added cautiously until the end-point is reached. Completion of the titration should always be with the decimal salt solution. Some confusion in judgment of the end-point may arise, on account of the fact that an excess of sodium chloride produces turbidity. The appearance of the cloud so produced is characteristic, and can be distinguished after some practice from that exhibited when silver is still in excess. If bromide standard and decimal solutions are used, excess of the reagent produces a turbid film only after long standing.

The silver value in milligrams of the standard solution, plus the number of cc. of decimal salt solution which produced a precipitate, minus the number of cc. of decimal silver solution added, gives the amount of silver in the quantity of sample weighed out.

The result calculated to milligrams silver per gram of sample is customarily reported in the case of silver bullion as points fineness.

The accuracy of the method is limited by the quality of pipette and the skill of the operator. With a pipette which delivers accurately an experienced operator can speedily make analyses in which the error is only of the order of plus or minus 0.1 milligram of silver. In the comparison of purity of samples of pure silver, it is customary to carry out determinations to the limit of the known accuracy of the pipette delivery.

NOTES. If the amount of mercury present is very small, addition of 20 cc. of a saturated solution of sodium acetate and several cc. of acetic acid before introduction of the standard salt solution will prevent precipitation of chloride of mercury. When the quantity of mercury is so large that this method fails, the quantity of silver weighed out is heated several hours at a red heat in a small covered crucible surrounded by coarsely powdered charcoal within a covered crucible of larger size.

When tin is known to be present [1] in the bullion to the extent of less than 5%, 2 grams tartaric are added to the assay bottle and dissolved with 3 or 4 cc. hot water. When the liquid is cool, 10 cc. nitric acid (1.26 sp.gr.) are added and solution of the bullion effected by the action of acid without the aid of heat. Unless prevented from forming by addition of tartaric acid, metastannic acid stays in suspension and obscures the end-point. If more than 5% of tin is present, such an amount of the sample should be weighed out which will make the tin content of the assay less than 50 milligrams. A weighed amount of pure silver is added sufficient to make the total silver present in the assay slightly more than the silver value of the standard salt solution and the method of solution carried out as described.

No pipette is of use in the practice of the Gay-Lussac method which shows any tendency to spatter at the beginning or ending, or yields a quickly following or clinging drop at the completion of discharge. The film of liquid adherent to the inner surface of the body of a good pipette will drain without sign of rivulet effect and be retained by the capillary of the discharge tube for at least a minute.

Determinations can be made without the use of the pipette by introducing the precipitant in the form of a weighed amount of the standard solution or of finely powdered pure dry salt, after dilution of the silver solution to about 125 cc. The

[1] L. E. Salas, Bull. A. I. M. E., **68**, 267.

ilver value of the salt should be determined by carrying out the operations of he method on pure silver.

Combination Methods

Combination of the operations of the Gay-Lussac and Volhard methods have been devised to avoid the tediousness incident to the performance of the Gay-Lussac method by the unexperienced. By the modified methods the amount of sample to be weighed out is determined by preliminary assay, and is dissolved in the same manner as in the practice of the Gay-Lussac method, but with the added precaution to decompose nitrous acid in the silver solution by gentle boiling when completion of the titration is to be accomplished by the Volhard method.

The operation of the combination methods consists briefly of precipitation of all but a few milligrams of silver by a standard solution of alkali thiocyanate, chloride or bromide added from the Stas pipette and estimation of the excess of silver with a decimal solution of thiocyanate or by a colorimetric or nephilometric method.

The procedure favored by the writer is to use a standard solution of potassium bromide as the pipette precipitant. After the liquid is cleared by shaking, it is decanted as completely as possible into a 500-cc. Erlenmeyer flask. The precipitate is washed by five 30-cc. portions of water containing a little nitrous-free nitric acid, each portion being shaken before decanting. Using the same amount of ferric indicator as in the check assays, decimal thiocyanate solution is added until not a very deep tint remains permanent after vigorous agitation. Decinormal silver solution is then added until the tint is discharged. When the assay is sufficiently free of copper or other colored salts to permit accurate matching of tints, the decanted liquid, which may contain particles of silver bromide without interference, is titrated with decimal thiocyanate to the appearance of a tint which will match that of the check assays. Except when colored salts are present in such quantity as to make recognition of the point of bleaching of the ferric thiocyanate coloration uncertain, the extreme range of error is 0.3 part per 1000.

For colorimetric method, see Smith, I.M.M Bull. No. 28. Determination of the residual silver in the filtrate from the thoroughly washed silver bromide precipitate is practicable by use of a suitable nephelometric apparatus.[1]

Denigè's Cyanide Method[2]

Silver which has been precipitated as chloride may be determined volumetrically by dissolving the precipitate with a measured quantity of a standard solution of potassium cyanide of about decinormal strength.

$$AgCl+2KCN=KAg(CN)_2+KCl.$$

Potassium iodide is then added and the excess of standard potassium cyanide solution determined by addition of potassium iodide and titration to the first appearance of a permanent precipitate with decimormal silver nitrate.

$$AgNO3+KI=AgI+KNO3;\ AgI+2KCN=KAg(CN)_2+KI.$$

NOTES. If the last portion of the precipitate of silver chloride dissolves with difficulty in the potassium cyanide, the liquid may be decanted into another beaker and solution completed with ammonia. The solutions are combined.

[1] Richards and Wells, Am. Chem. J., 235, 1903; Richards, ibid., 510, 1906; Richards, Com. 8th Int. Cong. Ap. Chem., Sec. 1, 423.

[2] Clennell, "The Cyanide Handbook," 433.

Extreme sensitiveness is claimed for the method if centinormal solutions be used and the opalescence indicating the end-point be detected by a beam of light across the liquid.

Miscellaneous Volumetric Methods

Silver may be determined by addition from a burette of a portion of a known volume of its neutral or slightly acid solution to a standard solution of sodium chloride which contains a little potassium chromate or bichromate and sufficient chlorine-free magnesium oxide emulsion to neutralize free acid. The end-point is indicated by the formation of a reddish or brown precipitate.

By Pisani's Method [1] a standard solution of iodide of starch is added to a very dilute neutral solution of nitrate of silver until the fluid becomes permanently blue.

By Vogel's Modification of Pisani's Method, [2] the silver solution, which may contain free acid, is titrated with standard starch iodide solution after addition of nitric acid containing nitrous acid.

By Andrews' Modification, [3] the standard solution of starch iodide is added to a solution of silver nitrate which contains so much ferrous nitrate or sulphate that iron will be in excess of the silver present.

$$2AgNO_3+2Fe(NO_3)_2+I_2=2AgI+2Fe(NO_3)_3$$

By Gooch and Bosworth's Method, [4] silver is determined by precipitating with an excess of potassium chromate, dissolving the precipitate in ammonia, reprecipitating by boiling to low volume and determining iodometrically either the chromate ion combined with the silver, or that remaining after precipitating the silver with a known amount of standard potassium chromate.[5]

Nephelometric Method

This method is practicable for the determination of a small concentration of silver in a clear and colorless liquid. Less than 2 milligrams of silver can be estimated with considerable accuracy by matching the opalescence produced by a drop of hydrochloric acid with that from a known quantity in a liquid of the same volume, depth and temperature. Intensity of opalescence attains the maximum in about five minutes after precipitation. Standard silver solution is made by dissolving 500 milligrams standard silver (see Preparation at close of chapter) with several cc. of dilute nitric in a liter flask and making the solution up to the mark. For most technical determinations the apparatus may consist of clear glass cylinders (color tubes) of suitable size. More accuracy can be arrived at by use of a nephelometer of refined construction, for example [6] the combination of a projection lantern and a Duboscq colorimeter.

Preparation of Pure Silver. The volumetric methods used for the determination of high percentages of silver, employ solutions which should be standardized by metal of the highest purity. For the preparation of this metal, the electrolytic method as described below is preferred by laboratories which are suitably equipped.

[1] Robière, Bull. Soc. Chim., **17**, 306, 1915; J. S. C. I., Oct. 30, 1915, 1073.
[2] Fresenius, "Quantitative Analysis."
[3] Zeit. für Anorg. Chem., **26**, 175.
[4] Am. J. Sci., **27**, 302.
[5] Am. Chem. Soc. Chem. Abs., Aug. 10, 1909, 1735.
[6] Wells, Am. Chem. J., **35**, 99, 508; Richards, Am. Chem. J., **35**, 510; Dienert, Compt. rend., **158**, 1117.

For the manufacture of a large quantity—several pounds—a basket-like support or the anode is made of several glass rods bent so that they will hang from the rim of . tall 1000-cc. or larger beaker or battery jar and dip into the receptacle about an inch.

Smaller anodes may be supported by the positive wire or by a cloth bag fixed in place by a string under the flare of the rim of the beaker. In any arrangement for the support of the anode, allowance of room should be made for the introduction and free movement of an L-shaped stirring rod.

The cathode may consist of sheet silver or of platinum foil, and lies flat on the bottom of the beaker. The immersed length of the silver or platinum wire leading from the cathode should be covered with rubber tubing.

Commercial silver, usually about 999 fine, may be used for the anode, but by retreatment of the deposit, very impure silver may be used, providing that the quantity of tellurium present is very low. The presence of tellurium will exhibit itself in the impossibility of obtaining the desired coarsely crystalline deposit.

Tellurium in moderate quantities may be removed by melting the silver in a crucible or scorifier, adding niter, permitting the silver to nearly freeze, raising the temperature and pouring into a hot crucible or scorifier in which the operation is repeated, preferably in a muffle furnace, until the surface of the silver is without streaks or spots when cooled to near freezing. An oxidizing atmosphere about the molten metal should be maintained. On the basis of 172 grams silver per cubic inch an anode mould for any convenient amount of silver may be shaped from 4-in. pieces of 1-in. square rod on a smooth iron plate. Just before the anode bar sets in the mould, a silver terminal strip or wire is plunged into it.

After coating the contact wire or strip and the surface of the anode about it with sealing wax, the anode is wrapped with filter paper, held firmly in place by string or rubber bands. If the anode weighs half a pound or more, the anode is also wrapped with cotton flannel which has been washed with water until free of chloride. A porous dish, cylinder or filter cone can be used instead of filter paper and cloth.

The electrolyte contains about 4% of C.P. silver nitrate and half a per cent of chlorine-free nitric acid in distilled water, and fills the beaker or jar so it wets only the lower surface of the anode.

The current, of about 0.1 ampere per square inch of cathode surface at the start, is raised after deposition has proceeded for a few minutes to the limit at which a coarsely crystalline deposit can be maintained.

Inasmuch as the electrolysis proceeds at a rate of 4 grams per ampere hour, some attention is required to break up short circuits and to pack down the rather bulky deposit. The deposit, if coarse, can be washed very easily free of electrolyte, and after heating to near redness is in the form preferred for use by many assayers.

Other methods which may be employed consist of dissolving the crude silver with nitric acid about 1.20 sp.gr. or with hot concentrated sulphuric acid, if platinum is present, separating the gold and platinum by filtration, precipitating AgCl with not too large an excess of HCl, stirring the precipitate until it coagulates, washing repeatedly with hot water until a washing is obtained which shows no precipitate with H_2S, reducing the silver chloride by contact with pure zinc, wrought iron or the silver terminal of a carbon-silver couple aluminum foil, and washing with hot dilute HCl until a test of the decanted liquid indicates absence of the precipitating element. The dried silver, mixed with about 1% of dry sodium carbonate, is packed into a clay crucible, the inside of which has been glazed with borax glass and covered with a layer of crushed charcoal.

The sodium carbonate is omitted in case it is desired to melt silver refined by electrolysis.

The silver melted in the tightly covered crucible is poured into an iron mould which has been chalked or black leaded.

By Knorr's method,[1] a solution of silver nitrate from which excess of nitric acid has been removed by evaporation is freed of metallic impurities by adding enough sodium carbonate to precipitate one-tenth of the silver, boiling and filtering. The silver in the nitrate is precipitated by sodium carbonate and the precipitate decomposed without addition of reducing reagent, by melting in a crucible. Excess sodium carbonate carried down with the precipitate of silver carbonate will cover the fusion and such as adheres tightly to the metal is readily removed by hydrochloric acid. The metal should be smelted under charcoal.

[1] Liddell, " Metallurgists and Chemists' Handbook."

If tne cover of the charcoal is omitted or burned away during the fusion, the molten metal is capable of absorbing oxygen from the atmosphere to the extent ot about 0 25% of its weight. This gas is expelled during the passage of the metal into the solid state and produces a casting which cannot be rolled into smooth sheets

The most convenient size and shape of castings for rolling is but little larger than a lead pencil. Before rolling, the casting is cleaned of particles of the mould wash After rolling to about cardboard thickness, the sheets may be cut up into strips of convenient size and length, then digested with dilute hydrochloric acid (1 to 5 of water) washed with ammonia and finally with pure water.

The silver then should be dried and annealed by heating to redness. It is best preserved in a glass-stoppered, salt-mouth bottle and should be exposed to laboratory atmosphere as little as possible.

The purity of each batch of silver made should be compared by use of the Gay-Lussac method with standard silver, the purity of which has been determined by analysis of a 50- or 100-gm. portion for Se and Te, As, Sb, Pb, Cu, Au, and the element employed in reducing silver chloride, if the reduction method was followed in the manufacture of the metal.

STRONTIUM

WILFRED W. SCOTT

Sr'', *at.wt.* 87.63; *sp.gr.* 2.54; *m.p.* 900° C; *oxides* SrO *and* SrO_2.

DETECTION

Strontium is precipitated with barium and calcium, in the filtrate, from the ammonium sulphide group, by addition of ammonium carbonate to the ammoniacal solution. The precipitate is dissolved in acetic acid and treated with potassium dichromate, and the barium filtered off as $BaCrO_4$. Strontium and calcium in the filtrate are separated from the excess of potassium chromate by reprecipitation as carbonates by the addition of ammonium carbonate, the precipitate again dissolved in acetic acid and the excess of free acid neutralized with ammonia. Strontium may now be precipitated from the concentrated solution by boiling with an equal volume of a saturated solution of calcium sulphate.

Sodium Sulphate Test. A saturated solution of the salt added to a solution containing strontium chloride, made strongly acid with acetic acid, and the mixture boiled, will produce a distinct precipitate if strontium exceeds 0.0015 normal. Calcium does not precipitate until 1.3 normality is reached.[1]

Flame Test. Strontium, preferably in the form of the chloride in a hydrochloric acid solution, placed on a platinum loop and held in a colorless flame, colors the flame crimson. (Lithium gives a red color, calcium a yellowish-red.) The test is best confirmed by means of the spectroscope.

The Spectra of Strontium. Eight bright bands; 6 are red, 1 orange, 1 blue. Two of these, known as strontium β and γ, are red, the orange is strontium α and the blue strontium δ. The delicacy of the test is 0.6 milligram Sr per cc. The test is very much more delicate with the arc spectra, e.g., 0.03 milligram Sr per cc. See chapter on barium, Preliminary Tests under Separations.

ESTIMATION

Strontium never occurs free in nature. It is found principally in the ores celestine, $SrSO_4$, and strontianite, $SrCO_3$. It generally accompanies calcium in the various forms of calcite and aragonite. It occurs with barium in baryto-celestine, and is found in barytes. It also occurs associated with barium as a silicate in brewsterite, $Al_2O_3 \cdot H_4(BaSr)O_3 \cdot (SiO_2)_6 \cdot 3H_2O$. It is found in traces in certain mineral waters and in sea-water.

The compounds of strontium are used for medicinal purposes; for red fire in pyrotechnics; for the manufacture of iridescent glass; the dioxide for bleaching purposes; the sulphide for luminous paint; the hydroxide for refining of beet-root sugar, being preferable to lime, as the saccharate of strontia is more granular.

[1] J. D. Hinds, Jour. Am. Chem. Soc., **36**, 301, 1911.

Preparation and Solution of the Sample

The following facts regarding solubility may be of value in the determination of strontium. One hundred cc. of water dissolves 0.4 gram $Sr(OH)_2$. The hydroxide is less soluble than that of barium. The peroxide dissolves to the extent of only 0.008 gram per 100 cc. 20° C. One hundred cc. of water dissolves 0.0011 gram [1] $SrCO_3$ (18°); 0.0114 gram $SrSO_4$ at 18° and 0.0104 at 100°; the presence of sulphuric acid decreases this solubility, i.e., 0.00083 gram $SrSO_4$; 0.0051 gram $SrC_2O_4 \cdot H_2O$ at 18° and 5 grams at 100° C.; the presence of oxalic acid decreases this solubility. The sulphate dissolves in concentrated sulphuric acid, and is appreciably soluble in HCl, HNO_3, $HC_2H_3O_2$, NH_4Cl, NH_4NO_3, NaCl, $MgCl_2$. The carbonate and oxalate are soluble in mineral acids.

The procedure for the treatment of ores and strontium products is the same as those described for barium and calcium. We refer to the chapters on these elements for the preparation of the strontium solution.

SEPARATIONS

Separation of Strontium from Magnesium and the Alkalies. The procedure is the same as the one given in detail under barium for the separation of the alkaline earths from magnesium and the alkalies. Either the oxalic acid method or precipitation of strontium as a sulphate in presence of alcohol will accomplish this separation. If a sulphate precipitation is made it will be necessary to fuse the sulphate with sodium carbonate to get it into solution or to effect further separation from members of the ammonium carbonate group, should these be present.

Separation of Strontium from Calcium.[2] Strontium and calcium are converted into the nitrates and taken to dryness and all water expelled by heating to 140° C. for an hour or more. The nitrates are now extracted with equal parts of absolute alcohol and anhydrous ether or by boiling with amyl alcohol at 130° C. (hood). Strontium remains insoluble and calcium goes into solution as the nitrate. Strontium nitrate may require further solution in water, evaporation to dryness, heating and extraction to remove calcium completely, should this be present in large excess. The nitrate of strontium is dissolved in water and strontium determined by one of the procedures given later. See detailed procedure for separation under Barium.

Separation of Strontium from Barium. The procedure is given in detail under chapter on Barium. In brief one of the following methods may be used: Strontium and barium in a mixture of the nitrates are separated from calcium by treatment with ether-alcohol mixture, in which $Ba(NO_3)_2$ and $Sr(NO_3)_2$ are insoluble. The nitrates dissolved in water are separated by precipitating barium as $BaCrO_4$ from a faintly acetic acid solution, strontium remaining in solution.

If preferred, barium may be first removed as a chromate, strontium and calcium precipitated from an ammoniacal solution by $(NH_4)_2CO_3$ as carbonates, the carbonates converted to nitrates and $Sr(NO_3)_2$ separated from $Ca(NO_3)_2$ in an ether-alcohol solution or by amyl alcohol. Details of the separations are given under Barium.

[1] Treadwell claims solubility = 0.00055, i.e., 1 part $SrCO_3$ in 18,045 parts of water.

[2] Advantage may be taken of the insolubility of strontium sulphate in ammonium sulphate in separating it from the soluble calcium salt.

GRAVIMETRIC METHODS

Strontium may be conveniently determined either as the sulphate, the carbonate or as the oxide.

Determination as Strontium Sulphate, $SrSO_4$

Procedure. A slight excess of dilute sulphuric acid is added to the neutral solution of strontium, and then an equal volume of alcohol. The mixture is stirred well and settled for several hours, or overnight, if more convenient. The precipitate, $SrSO_4$, is filtered onto a small ashless filter and washed first with 50% alcohol containing a little sulphuric acid, then with alcohol until free of acid. The precipitate is dried and the paper and the greater part of the salt ignited separately, then combined and weighed as $SrSO_4$.

Factors. $SrSO_4 \times 0.477 = Sr$, or $\times 0.8037 = SrCO_3$, or $\times 0.5642 = SrO$.

Determination as Strontium Carbonate

Strontium carbonate is not readily decomposed by ignition as is calcium carbonate, so that its determination in this form may be satisfactorily made.

Procedure. The carbonate is precipitated by adding ammonium carbonate in slight excess [1] to the ammoniacal solution of strontium, heated nearly to boiling. The solution is allowed to stand for several hours and filtered cold. The washed strontium carbonate and filter are ignited gently and the cooled residue weighed as $SrCO_3$.

Factors. $SrCO_3 \times 0.5935 = Sr$, or $\times 1.2443 = SrSO_4$, or $\times 0.702 = SrO$.

Determination as Oxide, SrO

Strontium is precipitated as the oxalate by addition of ammonium oxalate to the slightly ammoniacal solution. The precipitate is filtered and washed with water containing ammonium oxalate. The residue is ignited and weighed as SrO.

Factors. $SrO \times 0.8456 = Sr$, or $\times 1.7726 = SrSO_4$, or $\times 1.4245 = SrCO_3$.

VOLUMETRIC METHODS

The volumetric methods for determining strontium presuppose its isolation from other elements.

Alkalimetric Method, Titration with Standard Acids

Either the carbonate or the oxide of strontium may be titrated with standard hydrochloric or nitric acids. The compound is treated with a known amount of standard acid added in excess, using methyl orange indicator. The solution is heated below boiling to complete the reaction and, upon cooling, the excess of acid is titrated with standard alkali.

One cc. normal acid = 0.04381 gram Sr, or 0.05181 gram SrO, or 0.07381 gram $SrCO_3$.

[1] N. B. Avoid a large excess of $(NH_4)_2CO_3$. NH_4Cl has a solvent action on $SrCO_3$.

Titration of the Chloride with Silver Nitrate

Strontium chloride, free from other chlorides, may be determined indirectly by titration of its combined chlorine with silver nitrate by Mohr's method, using potassium chromate indicator. One cc. N. $AgNO_3 = 0.04381$ gram Sr.

The oxide or carbonate is slightly supersaturated with hydrochloric, then taken to dryness and heated at 120° C. in the air bath to expel the excess of acid. Chlorine is determined on an aliquot portion.

SULPHUR

WILFRED W. SCOTT

S, *at.wt.* 32.07; *sp.gr.* 2.035; *m.p.* 111°; *b.p.* 444.53°; *oxides* S_2O_3, SO_2, SO_3, S_2O_7; *principal acids* $H_2S_2O_4$, H_2SO_3, H_2SO_4, $H_2S_2O_3$, *and* $H_2S_2O'_8$.

DETECTION

The following tests include the detection of free sulphur and its more important combined forms.

Element. Sulphur is a polymorphous, yellow, brittle, odorless and tasteless solid; existing in the rhombic, monoclinic and triclinic crystalline forms, and also in an amorphous state. At 111° [1] it melts to a pale yellow liquid; at 180° it thickens to a dark gum-like material, containing a large percentage of amorphous sulphur; at 260° it becomes a liquid again, and at 444.53° it boils, giving off a brownish-red vapor.

Heated in the air sulphur burns with a blue flame, and is oxidized to SO_2, a gas with a characteristic pungent odor. This gas passed into a solution of potassium permanganate will decolorize it, if SO_2 is in excess of the amount that will react with the $KMnO_4$ in the solution.

If sulphur is dissolved in a hot alkali solution and a drop of this then placed on a silver coin, a stain of black Ag_2S will be evident, due to the action of the sulphur.

Sulphides. Hydrogen sulphide, H_2S, is liberated when a sulphide is treated with a mineral acid. This gas blackens moist lead acetate paper. H_2S has a very disagreeable odor, which is characteristic.

Sulphates. A white compound, $BaSO_4$, is precipitated in presence of free hydrochloric acid when a solution of barium chloride is added to a solution of a sulphate.

Insoluble sulphates are decomposed by boiling or fusion with alkali carbonates, forming water-soluble alkali sulphates.

Sulphites. Sulphur dioxide, SO_2, is evolved when a sulphite is treated with hydrochloric acid. The odor of the gas is characteristic.

Sulphur dioxide decolorizes a solution of potassium permanganate. (Use very dilute solution.)

Sulphites are distinguished from sulphates by their failure to form a white precipitate, when barium chloride is added to the solution acidified with hydrochloric acid; also by the fact that H_2S is formed when zinc is added to a solution of a sulphite, acidified by hydrochloric acid.

Thiosulphates. Sulphur dioxide is evolved and free sulphur precipitated when a thiosulphate is acidified with dilute mineral acids. In presence of oxidizing agents sulphides will also liberate free sulphur.

Thiosulphates are strong reducing agents.

[1] U. S. Bureau of Standards gives the following melting-points: $S_1 = 112.8°$, $S_2 = 119.2$, $S_3 = 106.8$. Circular 35 (2d Ed.).

ESTIMATION

The determination of sulphur may be required in a great variety of substances, minerals, rocks, sulphur ores, acids, salts, water, gas, coal and other organic matter.

The substance occurs in nature principally in the following forms:

Element. Found free, generally mixed with earthy matter. The commercial product is exceedingly pure and may contain over 99.5% S.

Sulphur Dioxide. The gas, together with free sulphur, is found in volcanic regions.

Hydrogen Sulphide. Occurs in mineral waters and in the air, from decaying organic matter.

Sulphide Ores. Iron pyrite, FeS_2 (30 to 50% S); ferro ferric sulphide, $Fe_2O_3 \cdot 5FeS$; pyrrhotite, Fe_7S_8; copper pyrites, $CuFeS_2$; realgar, As_2S_2; orpiment, As_2S_3; galena, PbS; cinnabar, HgS; zinc blende, ZnS.

Sulphate Ores. Gypsum, $CaSO_4 \cdot H_2O$, very abundant; barytes, or heavy spar, $BaSO_4$; celestite, $SrSO_4$; kieserite, $MgSO_4 \cdot H_2O$; bitter spar or Epsom salts, $MgSO_4 \cdot 7H_2O$; Glauber salt, $Na_2SO_4 \cdot 10H_2O$; sulphates of alkalies in animal and plant fluids.

The gravimetric determination of sulphur, by procedures of technical importance, depends upon its precipitation as barium sulphate, $BaSO_4$, after converting it into sulphuric acid, or a soluble sulphate, if not already in this form. Oxidation of free sulphur, sulphides, sulphites, metabisulphites, thiosulphates may be accomplished by either dry or by wet methods, details of which are given under subsequent procedures. When present as a sulphide, or having been converted to this form, the substance may be evolved as hydrogen sulphide, the gas absorbed by a suitable agent, and after oxidation it may be determined by precipitation as $BaSO_4$ and thus weighed.

The volumetric methods of determining sulphur depend upon titration with oxidizing agents, or by acids, or by alkalies, according to the form of the sulphur compound, or by means of a substance forming an insoluble compound with sulphuric acid. For example sulphides are treated with a strong mineral acid (HCl), the evolved H_2S absorbed in a suitable reagent, and the sulphide formed is titrated with standard iodine. Sulphites may be determined either by oxidation with iodine or by titration with an acid in presence of methyl orange. Acid sulphites or metabisulphites may be determined by the iodine titration or by titration with an alkali in presence of phenolphthalein. Thiosulphates are titrated with iodine. Soluble sulphates may be titrated with standard barium chloride or chromate, added in slight excess, and the excess estimated by titration.

Standard procedures are given, covering the more important forms which commonly concern the analyst.

Preparation and Solution of the Sample

In the preparation of the sample the following facts regarding solubility of sulphur and its combination should be kept in mind.

Element. The crystalline forms are soluble in CS_2, the monoclinic form is soluble also in alcohol, chloroform and benzol. Yellow amorphous and plastic sulphur are insoluble in CS_2. Sulphur precipitated by the action of HCl

upon $(NH_4)_2S_x$ is soluble in benzol. The element is soluble in hot hydrates of sodium, potassium, barium and calcium, forming polysulphides and thiosulphates.

Sulphide. Sulphides of Na, K, Cs, Rb, Ca, Sr, Ba, Mg, Mn, Fe are soluble in dilute mineral acids. The sulphides of Ag, Hg, Pb, Cu, Bi, Cd, Co, Ni require strong acids for decomposition. These are also insoluble in sodium hydroxide and potassium hydroxide solutions. As, Sb and Sn sulphides are insoluble in dilute acids, but soluble in alkalies.

Sulphate. With exception of $BaSO_4$, $CaSO_4$, $SrSO_4$ and $PbSO_4$, sulphates are soluble in water.

Thiosulphate. Nearly all are soluble in water.

Sulphite. With exception of the sulphites of the alkalies, sulphites of the metals are difficultly soluble in water, but readily decomposed by acids.

Decomposition of Sulphur Ores

The wet procedure for oxidation and decomposition of sulphur ores is given in detail under the Gravimetric Methods, page 396. This process is used for the valuation of the ore, and is applicable to a wide range of substances.

Fusion Method. One gram of the finely ground ore (80 mesh) is intimately mixed with 6 grams of zinc oxide-sodium carbonate mixture (4 parts ZnO+1 part Na_2CO_3), placing 2 grams more of the mixture over the charge. The material is fused and sulphur extracted according to the procedure described for coal—Eschka's method.

Sulphur in Coal, Eschka's Method

One gram of coal is intimately mixed with 3 grams of Eschka's compound, consisting of 2 parts of porous, calcined magnesia and 1 part of anhydrous sodium carbonate. The mixture, placed in a platinum crucible, is covered with about 2 grams more of Eschka's compound. The charge is placed in an open platinum crucible, which is protected from the flame by a shield, as shown in Fig. 65. If possible, a sulphur-free flame should be used to avoid contaminating the material. With proper precautions, the shield will prevent this. Heating in a crucible electric furnace completely avoids sulphur contamination. The mixture is heated very gradually, to drive off the volatile matter, the charge being stirred frequently with a platinum wire to allow free access of air. The heat is increased, after half an hour, to a dull redness. When the carbon has burned out, the gray color having changed to a yellow or light brown, the heat is removed and the crucible cooled.

The powdered fusion is digested with 100 cc. of hot water for half an hour, and the clear liquor decanted through a filter into a beaker. The residue is washed twice more with hot water, by decantation, and finally on the filter, until the volume of the total filtrate amounts to about 200 cc. About 5 cc. of bromine and a little hydrochloric acid are added, and the solution boiled. Sulphuric acid is now precipitated as $BaSO_4$ by addition of barium chloride to the hot solution, and sulphur determined by the first of the gravimetric procedures.

Sulphur in Rocks, Silicates, and Insoluble Sulphates

The material in finely powdered form is fused in a large platinum crucible with about six times its weight of sodium carbonate (sulphur free) mixed with about 0.5 gram of potassium nitrate. The charge is protected from the flame

by an asbestos board or silica plate with an opening to accommodate the crucible snugly, as shown in Fig. 65. The fusion is extracted with water, the filtrate evaporated to dryness and silica dehydrated. The residue is moistened with strong hydrochloric acid, then taken up with a little water, boiled free of CO_2, and silica filtered off. The filtrate contains the sulphate, which is now precipitated as barium sulphate according to one of the standard procedures.

Barium Sulphate. This is transposed by fusion with sodium carbonate, as stated above. Barium carbonate remains in the water-insoluble residue. It is advisable to wash the residue in this case with hot sodium carbonate solution, to insure complete removal of the sodium sulphate. The filtrate is acidified with HCl, boiled free of CO_2 and $BaSO_4$, then precipitated.

Lead Sulphate. This may be transposed by digesting the compound with a strong solution of sodium carbonate saturated with CO_2, keeping the solution at boiling temperature for half an hour or more. The sulphate will be in solution and the lead is precipitated as the water-insoluble carbonate.

Strontium or calcium sulphates may be transposed by the procedure described for lead.

SEPARATIONS

Substances Containing Iron

In precipitating barium sulphate, in presence of ferric salts, from hot solutions by the gravimetric procedure commonly followed, considerable iron is carried down by the precipitate. Since $Fe_2(SO_4)_3$ loses SO_3 upon ignition, and since Fe_2O_3 weighs much less than $BaSO_4$, low results will be obtained. Hence the removal of iron is necessary, or a method should be followed in which iron does not interfere. It is found that barium sulphate precipitated from a large volume of cold solution, in which the iron has been reduced to ferrous condition, is free from iron. Details of this procedure are given in the second of the gravimetric methods, page 396.

If sulphur is to be precipitated from hot solution of comparatively small volume (200 to 400 cc.), it is necessary to remove iron. This is accomplished by precipitating this as $Fe(OH)_3$ by addition of ammonium hydroxide in decided excess (5 to 10 cc. excess of strong NH_4OH, sp.gr. 0.90). If the solution is barely neutralized with ammonia, the iron hydroxide carries down considerable of the sulphate. Even with the precaution recommended some of the combined sulphuric acid is occluded by the precipitate, so that it is necessary to recover this by dissolving the precipitate with hydrochloric acid and reprecipitating the ferric hydroxide with an excess of ammonia. The combined filtrates are now treated with barium chloride, upon acidification with hydrochloric acid, according to the procedure first given, page 395, and the sulphate determined.

Separation of Sulphur from Metals Forming an Insoluble Sulphate

This is accomplished by fusion of the compound with sodium carbonate and extraction of the mass with water. The metal remains with the residue and the sulphate of the alkali passes into solution. For details see subject under Preparation and Solution of the Sample, page 392.

Nitrates and Chlorates. These are carried down with the precipitate as barium salts if they are present in appreciable amount. They may be removed from the solution by evaporation to dryness with hydrochloric acid.

Silica. Silica will be carried down with the barium sulphate precipitate if present in appreciable amounts. It is removed by evaporation of the solution with hydrochloric acid, dehydrating the silicic acid, taking up with HCl and water and filtering.

Ammonium and Alkali Salts. These have a negligible effect on the precipitate of $BaSO_4$ if this is precipitated from a large volume, according to the second gravimetric procedure.

GRAVIMETRIC DETERMINATION OF SULPHUR

Precipitation as Barium Sulphate

Preliminary Remarks. The procedure depends upon the insolubility of barium sulphate, $BaSO_4$, in neutral or slightly acid solutions. It was formerly the general practice to precipitate the sulphur by adding a 10% barium chloride solution to the hot sulphate solution, which had been diluted from 200 to 400 cc., according to the amount of sulphur that was present (not over 0.2 gram sulphur per 100 cc.), containing 1 to 3 cc. of free concentrated hydrochloric acid per 100 cc. of solution. Special precautions were given to have the solution boiling hot, and to avoid having a volume of over 400 cc., a smaller sample being taken in high sulphur ores, rather than increase the volume. Extended experiments have shown that it is preferable to precipitate the sulphate from a large volume of cold solution. The product obtained is less apt to occlude impurities, the crystals are larger than those obtained in hot concentrated solutions, and do not pass through the filter. Precipitation may be made in presence of large amounts of iron, copper and other impurities. The procedure requires large beakers of 2- to 2½-liter capacity, special precipitating cups, and a suction apparatus, as shown in Figs. 60, 61, 62 and 63. This apparatus may not always be available, and occasionally it is advantageous to precipitate the sulphur in a small volume, specially when the sulphur content of the material is low, hence, although the second procedure is generally recommended, the older method is also included.

I. Precipitation of Barium Sulphate from Hot Solutions

Procedure. The sulphur should be present in solution either as free sulphuric acid or as a sulphate salt. The solution is made acid by addition of hydrochloric acid (phenolphthalein indicator), and then 4 cc. added in excess (HCl, sp.gr. 1.2). After diluting to a volume of 400 cc. with hot water, the mixture is heated to boiling, and a 10% solution of barium chloride added in a fine stream,[1] through a funnel with a capillary stem, or from a burette, at the rate of 10 cc. in two to ten minutes. The reagent is added in slight excess of that required to react with the sulphuric acid or sulphate. (Ten cc. of 10% barium chloride solution will precipitate 0.1416 gram of sulphur.) The beaker is placed on a steam bath and the pre-

[1] E. Hintz and H. Weber recommend adding 100 cc. of N/10 $BaCl_2$ solution, boiling hot, to the hot sulphate solution all at once in place of slowly, as recommended in general practice. (See Treadwell and Hall, "Analytical Chemistry," **2**, 3d Edition, p. 469.)

cipitate allowed to settle for about two hours. The solution is filtered through a fine grade of filter paper (B. & A. grade A, or S. & S. grade No. 90), or through a tared Gooch crucible. Since the precipitate frequently passes through the filter it is advisable always to pass the solution through the same filter a second time. The precipitate is washed ten times with hot water, then dried, and ignited gently over a Bunsen burner, or in a muffle, for half an hour. (Blasting is not necessary, nor desirable.) The white $BaSO_4$ is cooled in a desiccator, and then weighed. If a filter paper has been used in place of a Gooch crucible, the ignition is best made in a porcelain crucible,[1] with free access of air, the ignited sulphate, upon cooling, is brushed out of the crucible and so weighed.

Factors. $BaSO_4 \times 0.1373 = S$, or $\times 0.4202 = H_2SO_4$, or $\times 0.3766 = FeS$, or $\times 0.2744 = SO_2$, or $0.3430 = SO_3$, or $\times 0.4115 = SO_4$.

NOTE. If much iron or alumina is present it is advisable to precipitate the sulphate from a large volume, by the second method, rather than attempt to remove these substances. If $BaSO_4$ is present in the original material its weight should be included with that of the precipitate.

II. Precipitation of Barium Sulphate from Cold Solutions—Large Volume

Introduction. The method worked out by Allen and Bishop, General Chemical Company,[2] is especially adapted to the determination of sulphur in iron pyrites and materials high in sulphur, 30 to 50% sulphur, but by varying the amount of material used the range may be extended from smaller to greater amounts. The finely ground sample is oxidized by means of a mixture of bromine and potassium bromide, followed by nitric acid. The nitric acid is expelled by evaporation to dryness, followed by a second evaporation with hydrochloric acid, which dehydrates the silica. Iron is now reduced to the ferrous condition and the silica and residue, undissolved by addition of hot water and HCl, is filtered off. The sulphur is precipitated in a large volume of cold solution, by barium chloride solution, as $BaSO_4$ and so weighed.

Reagents. ***Bromine—Potassium Bromide Solution.*** 320 grams of potassium bromide are dissolved in just sufficient water to cause solution and mixed with 200 cc. of bromine, the bromine being poured into the saturated bromide solution. After mixing well the solution is diluted to 2000 cc.

Hydrochloric Acid, sp.gr. 1.20. ***Nitric acid,*** sp.gr. 1.42.

Aluminum Powder Free from Sulphur.

Barium Chloride, anhydrous, 5% solution; or crystals, 6% solution.

Procedure. ***Preparation of Sample.*** The sample ground to pass 80-mesh sieve is carefully mixed and quartered down to 10 grams. This is dried for one hour at 100° C. and then placed in a weighing tube.

A factor weight, 1.3738 grams of the sample, is placed in a deep Jena beaker, 300 cc. capacity, $2\frac{1}{2}$ by $4\frac{1}{2}$ ins.

Oxidation of Sulphur. Ten cc. of the bromine-potassium bromide mixture are added and the beaker covered with a dry watch-glass cover. After standing

[1] A platinum crucible will do.

[2] Paper before Eighth International Congress of Applied Chemistry: "An Exact Method for the Determination of Sulphur in Pyrites Ores," W. S. Allen and H. B. Bishop.

fifteen minutes in the cold bath (a casserole of water will do), with occasional shaking of the beaker, 15 cc. of strong nitric acid are added and the mixture allowed to stand fifteen minutes longer, at room temperature, and then warmed on an asbestos board on the steam bath until the reaction has apparently ceased and the bromine has been volatilized. The beaker is now placed within the ring of the steam bath so that the lower portion is exposed to steam heat. The solution is evaporated to dryness, the cover of the beaker being raised above the rim by means of riders (U-shaped glass rods), Fig. 60, 10 cc. of strong hydrochloric acid are now added and the solution again evaporated to dryness to expel the nitric acid. The silica is dehydrated by heating in the air oven at 100° C. for one hour, or overnight if preferred.

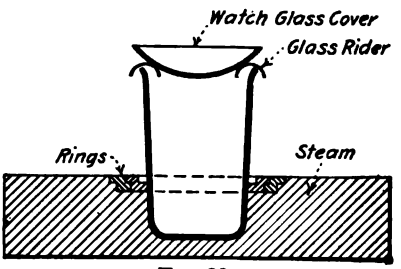


FIG. 60.

Reduction of Iron. Four cc. of hydrochloric acid (sp.gr. 1.20), followed five minutes later by 100 cc. of hot water, are added, the sides of the beaker and the cover being rinsed into the solution. The riders being removed, the sample is gently boiled for five minutes to insure the solution of the sulphate. After cooling for about five minutes, approximately 0.2 gram powdered aluminum is stirred into the solution, keeping covered during the intervals between stirring. When the iron has been reduced, the solution becoming colorless, the sample is filtered into a 2500-cc. beaker, through a 12½ cm. filter paper (S. & S. No. 590 or B. & A. No. A). The beaker should be copped out and the residue on the filter washed nine times with hot water, filling the filter funnel and draining each time.

Precipitation of the Sulphur. The solution in the large beaker is diluted to 1600 cc. with cold water and 6 cc. HCl (sp.gr. 1.20) added, and mixed by stirring. The barium chloride solution is now added by means of a special delivering cup (Figs. 61 and 62), which should drain at the rate of 5 cc. per minute. 125 cc. of barium chloride solution are added for ores containing 30 to 50% sulphur, the factor weight being taken. The solution is not stirred while the barium chloride is being added, but when the cup has drained, the solution is mixed by stirring. The $BaSO_4$ is allowed to settle, two or three hours being advisable, overnight being preferred.

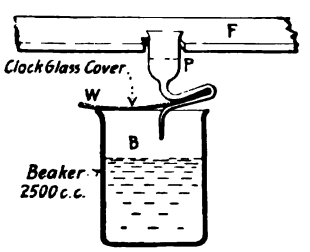


FIG. 61.

FIG. 62.

Apparatus for Precipitating Sulphur.

Filtration. The clear solution is filtered through a weighed Gooch crucible (35 cc.), using suction. This is best done by the automatic arrangement shown in Fig. 63. The beaker containing the solution is placed on a shelf; a siphon dipping to within half an inch of the precipitate at the bottom of the beaker is connected to the Gooch crucible by means of a tightly fitting stopper. The Gooch and thistle tube are best connected by heavy rubber tubing. The

suction flask, or bottle, should have a capacity of about 3 liters. A Geissler stop-cock passes through the rubber stopper in the suction flask to relieve the pressure when the Gooch is to be removed. The precipitate is washed onto the asbestos mat in the crucible and washed with cold water six times, the beaker being copped out as usual.

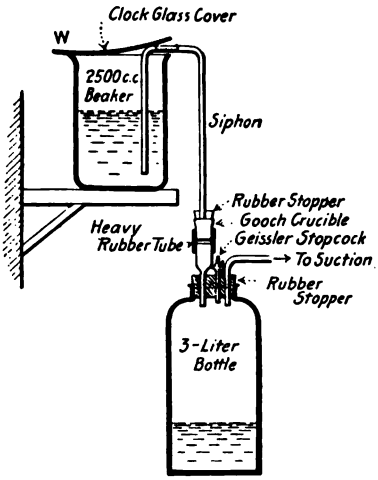


FIG. 63.—Apparatus for Filtering Barium Sulphate.

Ignition. The precipitate is dried by placing the crucible on an asbestos board over a flame for twenty-five minutes and then heated over a direct flame for thirty minutes.

Calculation. $BaSO_4 \times 10 =$ per cent S. (If factor weight is taken.)

Factor. $BaSO_4 \times 0.1374 =$ gram S.

Notes and Precautions

Although barium sulphate is only slightly soluble in water, it is appreciably soluble in the salts of the alkalies (Na, K and NH_4), and in a large excess of hydrochloric acid.

Barium sulphate occludes salts, especially nitrates and chlorides. Ferric chloride is carried down with this precipitate, though ferrous chloride is not; hence the reduction of iron is necessary. Occlusion of iron causes low results, as will be seen from the fact that with heating of $Fe_2(SO_4)_3$, SO_3 is volatilised, the salt decomposing to $Fe_2O_3 + SO_3$. With the iron reduced the precipitate burns perfectly white, whereas with ferric iron present the precipitate is invariably red or yellow. Aluminum powder used by W. H. Seamon,[1] for reduction of iron in determination of sulphur, suggested its value in the method above given.

Potassium bromide is added to the bromine mix as a diluent to prevent too vigorous a reaction. Cooling the solution is for the same purpose as a loss of sulphur will result if the reaction is violent. This is especially the case in pyrrhotite ore.

Otto Folin [2] shows that precipitation of $BaSO_4$ in a large volume of cold solution produces large crystals.

Mechanical loss and reduction of $BaSO_4$ is avoided by the Gooch crucible.

The method has been thoroughly tested in the laboratories of the Gen. Chem. Co. and has become a standard method for sulphur.

Evolution Method for Determining Sulphur in Iron, Steel, Ores, Cinders, Sulphides and Metallurgical Products

Introduction. The method depends upon the fact that hydrogen sulphide is evolved when a sulphide is acted upon by a strong acid such as hydrochloric acid. This gas, absorbed by a suitable reagent, may be determined gravimetrically [3] by weighing directly the precipitated sulphide, or by oxidation of either the hydrogen sulphide evolved or the sulphide formed in the absorbing reagent,

[1] Chemical Engineer, September, 1908.

[2] Journal of Biological Chem., 1, 131–159.

[3] *Gravimetrically.* (*a*) Evolution of H_2S into solutions of $ZnCl_2$, KOH, $KMnO_4$, $AgNO_3$, $Hg(CN)_2$, H_2O_2, Br+HCl and subsequent oxidation to sulphate when necessary, and precipitation as $BaSO_4$. (*b*) Absorption of H_2S by neutral or alkaline solutions of lead, oxidation of PbS to $PbSO_4$ and weighing as such. (*c*) Absorption of H_2S in solutions of $AgNO_3$, $CdCl_2$, and weighing the precipitated sulphide.

and precipitating sulphur as $BaSO_4$. It may be determined volumetrically [1] by titrating the precipitated sulphide with iodine or by titrating the acid, formed by the reaction, with standard caustic. The iodine and caustic titrations may be made on the same run, or the sulphide may be weighed and the filtrate containing the free acid titrated, thus double checking results. The following reaction takes place when the gas is evolved and absorbed by neutral cadmium sulphate:

$$H_2S + CdSO_4 = CdS \text{ precipitate} + H_2SO_4 \text{ free acid.}$$

The method is especially adapted to the determination of sulphur in iron and steel or in metallurgical products containing small amounts of sulphide. It may be applied to products containing larger amounts of sulphur as sulphides or sulphates, the latter condition requiring a special preliminary treatment.

The method is not applicable for determining free sulphur or sulphur in iron pyrites.

Reagents. ***Iodine Solution.*** Two strengths of this reagent should be at hand for general work:

For iron and steel and low sulphur briquettes, etc. = .01 to 0.5% S..... N/30 I
For sulphur products containing over 0.5% S..... N/10 I

Starch Solution. Made from a good grade of soluble starch, 1 gram per 200 cc. of water. Fresh solutions are desirable, as the deteriorated material produces a greenish-brown color in place of the delicate blue desired. Flocks of insoluble starch will cause the same difficulty.

Cadmium Chloride or Cadmium Sulphate Solutions. Ammoniacal Solution. Fifty-five grams of $CdCl_2 \cdot 2H_2O$ or 70 grams of the sulphate are dissolved in 500 cc. of distilled water. To this are added 1200 cc. NH_4OH (sp.gr. 0.90) and the solution diluted to 2500 cc. The solution is of such strength that 50 cc. will precipitate approximately 0.175 gram sulphur evolved as H_2S. This is equivalent to about 3.5% sulphur on a 5-gram sample.

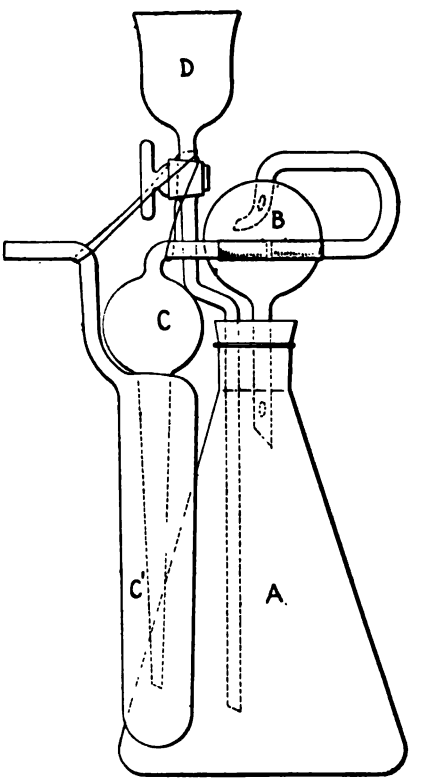


FIG. 64.—Scott's Apparatus for Determining Sulphur in Iron and Steel.[2]

[1] ***Volumetrically.*** (*a*) Absorption in a solution of KOH, $CdCl_2$ or $CdSO_4$, $ZnCl_2$ or $ZnSO_4$, Na_2HAsO_2 and titration with iodine solution. (*b*) Absorption in iodized KI and titration of the excess of iodine with $Na_2S_2O_3$ solution. (*c*) Absorption in a neutral solution of a metallic salt and titration of the liberated acid. (*d*) Absorption in caustic alkali and addition to an acid solution of a reducible salt, e.g., Fe_2O_3 and titration of the lower oxide, FeO.

[2] Apparatus designed by W. W. Scott.

Neutral Solution. To be used where titration with caustic is desired. Seventy grams of $CdSO_4$ are dissolved in water and made up to 2500 cc. The solution should be neutral to methyl orange, otherwise add the requisite amount of H_2SO_4 or NaOH necessary, determined by titration of an aliquot portion.

Hydrochloric Acid. One part concentrated acid to an equal volume of distilled water.

Sulphuric Acid. One volume of concentrated acid to four volumes of distilled water.

Reducing Mixture for Reduction of Sulphates. Five parts of $NaHCO_3$, 2 parts of C.P. aluminum powder and 1 part of pure carbon, best made by charring starch. A blank should be determined on this material and allowance made accordingly.

Stannous Chloride. Ten-per cent solution.

Fine Granular Aluminum or Zinc Metal. Sulphur free, 20 mesh.

Apparatus. The apparatus shown in the illustration, Fig. 64, is the author's[1] modification of the form used at Baldwin Locomotive Works. This consists of an Erlenmeyer flask *A* of about 500-cc. capacity with large base. With material in which violent foaming occurs, during the evolution of hydrogen sulphide, it is advisable to use a wash bottle with large base, in preference to an Erlenmeyer flask. Through a rubber stopper is inserted a thistle tube with glass stopcock *D*, by which the acid is introduced into the flask. The hydrogen sulphide passes through a potash connecting bulb with trap as shown. A hole blown in the side of the tube prevents liquid being swept through. Connected to the potash bulb is the absorption bulb *C*, which is suspended by a wire attached to the thistle tube. The apparatus is compact, so that on a large hot plate, 30 by 20 ins., a dozen outfits may readily be accommodated. With the use of this apparatus the writer has been able to make over seventy-five determinations of sulphur in steel in an ordinary day's run.

Preparation and Amount of Sample

The amount of material to be taken for the determination depends upon the sulphur content as shown by the following table:

Approximate % of Sulphur Present.	Amount to take for Analysis.
0.01 to 1	5 grams
1.0 to 10	1
10.00 to 30	0.5
Above 30	0.25

The class of material will govern the method of procedure.

Iron and Steel. A 5-gram sample of drillings or finely divided material is treated directly in the evolution flask with hydrochloric acid, 1 : 1, and the hydrogen sulphide absorbed in ammoniacal cadmium chloride. The sulphide formed is titrated with iodine.

Iron Ore Briquettes and Materials Containing Sulphates. Low Sulphur. *Preliminary Reduction.* A 5-gram sample is intimately mixed with an equal weight of reducing mixture ($NaHCO_3$+Al+C) and wrapped in a 9-cm. ashless filter. The charge is placed in a 50-cc. nickel crucible with cover. The crucible

[1] W. W. Scott.

i inserted half way into an asbestos board or perforated silica plate (see Fig. 65) nd after covering, placed over a low flame of a Méker blast burner. The ame of the blast is gradually increased during the first ve minutes and the charge blasted for about twenty inutes. The crucible will appear a bright red and car- on monoxide gas escaping from under the crucible lid ill burn. The loss of sulphur, however, is not appreci- ble. The crucible is cooled without removing the cover. When cold the fused mass is quickly pulverized and laced in the dry evolution flask containing a mat of luminum granules or C.P. zinc dust or granulated tin. Hydrogen sulphide is best evolved with hydrochloric cid to which 4 or 5 cc. of 10% stannous chloride has een added to reduce ferric iron. The gas is absorbed n ammonical cadmium chloride and the cadmium sulphide ormed titrated with iodine.

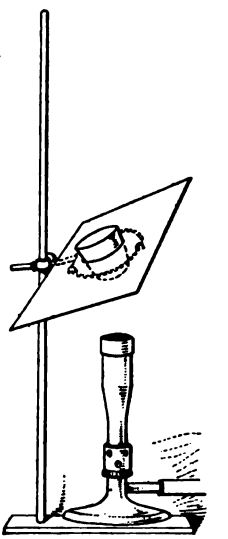


FIG. 65.

Iron Sulphide for Available H_2S. Since this product uns over 20% available hydrogen sulphide not over 0.5 gram sample should be taken. The H_2S is evolved by ddition of dilute sulphuric acid, 1 : 4, in place of hydro- hloric acid, and is absorbed by neutral cadmium sulphate. The acid formed by the reaction is titrated by standard N/10 NaOH.

Sodium Sulphide or Water-soluble Sulphides for Available H_2S. Ten grams dissolved in water and diluted to 1000 cc.; 50 cc. =(0.5 gram) taken for analysis.

Details of Procedure

Evolution of Hydrogen Sulphide. One-half to 1 gram of aluminum or zinc granules, 20 mesh, is placed over the bottom of the evolution flask and the sample placed above this mat of metal. The stopper with the thistle tube and condenser is inserted snugly into the neck of the flask. An absorption bulb containing about 20 cc. of distilled water is attached to the condenser. This bulb serves as a trap for the HCl that is driven out of the flask during the boiling. To this bulb is attached a second bulb containing 50 cc. of ammoniacal cadmium chloride. A third bulb may be attached if the sulphur content of the material examined is high; this, however, is seldom necessary when ammoniacal cadmium chloride is used. The rubber stopper and all rubber connections being air tight, 100 cc. of warm HCl, 1 : 1, is poured into the flask through the thistle tube, the stem of which should now dip well below the acid. The stopcock is closed during the violent action of the acid on the sample and opened when this has subsided. The acid trap prevents loss of H_2S through the thistle tube. The apparatus is now placed on the hot plate and the sample boiled vigorously for about twenty minutes. The flask is taken off the hot plate and the contents allowed to cool. At this stage it may be advisable to draw a current of air through the apparatus to sweep out any residual H_2S that may remain in the flask. Hydrogen gas is preferable to air.

Titration. (*a*) The contents of the bulbs are poured into a 600-cc. beaker containing about 400 cc. of distilled water. The bulbs are washed out first

with water and then with dilute acid. The excess of ammonia is neutralized with concentrated HCl, 5 cc. of starch solution added and the sulphide immediately titrated with standard iodine, additional hydrochloric acid being added from time to time during the titration to insure complete decomposition of the sulphide. The liquid appears yellowish red, orange, purplish red and finally a deep blue. Since the sulphide, when present in appreciable quantity, decomposes slowly, the solution should be strongly acid at the completion of the titration, and five minutes should be allowed for a permanent end-point.

Knowing the amount of iodine necessary, a check run may be made by adding to the neutral solution an excess of iodine followed by 5 cc. of starch solution and a large excess of concentrated hydrochloric acid. The excess of iodine is titrated with N/10 thiosulphate, $Na_2S_2O_3$, solution. (Arsenous acid will not do.) This procedure will prevent the loss of H_2S, which is apt to occur in samples high in sulphide.

(*b*) *An alternate method* is frequently advisable in high sulphurs. The precipitate is separated from the solution containing ammonia by filtration. The cadmium sulphide is now placed in the 600-cc. beaker with water and an excess of iodine run in. Starch is added, followed by hydrochloric acid. The excess of iodine is titrated with sodium thiosulphate, $Na_2S_2O_3$. By this method the heat action during the neutralization of ammonia is avoided and only the precipitate is titrated.

When the iodine titration exceeds 50 cc. of N/10 iodine, a smaller amount of the sample should be taken for analysis; the iodine titration for amounts of sulphur exceeding 0.1 gram is not satisfactory, owing to a fading end-point. The method for determining available hydrogen sulphide in high sulphide products, dealing with the titration of the free acid formed during the reaction, permits of larger samples being taken. Details of this method are given on page 407.

One cc. N/10 iodine = 0.001604 gram S.

Tenth Normal Equivalents

One cc. of N/10 iodine	= 0.001704 gram	H_2S
" "	= 0.004396 gram	FeS
" "	= 0.003904 gram	Na_2S
" "	= 0.003607 gram	CaS
" "	= 0.008471 gram	BaS
" "	= 0.00561 gram	Sb_2S_3
" "	= 0.011959 gram	PbS
" "	= 0.011634 gram	HgS
" "	= 0.004782 gram	CuS
" "	= 0.007224 gram	CdS
" "	= 0.004872 gram	ZnS
" "	= 0.003269 gram	Zn

Combustion Method for Evaluation of Sulphide Ores. When a sulphide ore (pyrrhotite) is heated to redness in presence of oxygen both sulphur dioxide and trioxide are evolved. The first may be absorbed in suitable reagents and estimated volumetrically or gravimetrically. The trioxide mist is best retained by asbestos and weighed. The combustion furnace with silica tube used for determinations of carbon is adapted for sulphide ores. The finely powdered

dry sample, spread in a thin layer in a 3-inch porcelain boat, is placed in the red hot tube and burned in a current of oxygen, which has been purified by passing through sodium hydroxide, strong sulphuric acid and phosphorus pentoxide. The trioxide mist is removed by passing the evolved gases through an asbestos filter (P_2O_5 bulb with asbestos in one arm adjacent to the combustion tube and P_2O_5 in the other). The SO_2 is absorbed in a mixture of bromine and nitric acid, and the sulphuric acid formed is titrated after removing the reagent by evaporation; or it is absorbed in an excess of standard iodine, the excess titrated with sodium arsenite or thiosulphate, and sulphur calculated. The iodine method is preferable to the bromine, as it is more rapid and the reagent less disagreeable to handle. The gravimetric method is the most reliable. The dioxide is absorbed in chromic acid (caustic will not give correct results owing to its affinity for carbon dioxide, a product of combustion of the free and combined carbon, that are generally present in sulphide ores. Pyrrhotite frequently contains as much as 1% carbon) and weighed. The combustion method cannot be recommended for extreme accuracy. The procedure may be used for the estimation of available sulphur, but does not give the total sulphur of the ore, since .2 to .5% remains in the cinder. Error may result from the following causes: (1) Incomplete combustion of the sulphur—due to sublimation of the sulphur to cooler zones of the combustion tube, and to a fine mist of sulphur passing unburned into the asbestos, where it is retained with SO_3 and weighed as such. (2) Error due to combined water of the ore. The results are apt to be .05 to 0.5% lower than those obtained by the barium sulphate procedures, the sulphur of the cinder being included with the available sulphur.

VOLUMETRIC METHODS FOR DETERMINING SOLUBLE SULPHATES

Combined sulphuric acid in soluble sulphates is best determined gravimetrically; occasionally, however, a volumetric procedure is of technical value. A number of volumetric methods are based on the insolubility of barium sulphate. Two general procedures deserve mention: addition of barium chloride in known amount in slight excess of that required by the sulphate, and titrating the excess either with a soluble carbonate or a chromate; or addition of barium chromate and titrating the alkali chromate formed by the reaction. The sulphate is also determined by precipitation with a weak organic base benzidine, added in form of the hydrochloride salt; the benzidine sulphate, filtered off, is titrated with caustic. The typical procedures given below will meet general requirements for the volumetric determination of sulphates.

Determination of Sulphur by Titration with Barium Chloride and Potassium Chromate—Wildenstein's Method Modified [1]

Reaction.

$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl$ and excess $BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$.

Procedure. The substance containing the sulphate in solution is diluted to 50 cc. in a small flask, acidified with hydrochloric acid, if necessary, heated to

[1] See "Volumetric Analysis," Sutton, 10th Ed., p. 350.

boiling, and precipitated with a slight excess of N/4 barium chloride added from a burette (1 cc. $BaCl_2$ = 0.01 gram SO_3). The precipitate settles rapidly, so that a large excess of the reagent may readily be avoided. The mixture is cautiously neutralized with ammonia, free from carbonate (CO_2 may be precipitated with $CaCl_2$ solution), the solution heated to boiling, and N/4 potassium chromate added from a burette in .5 cc. portions, each time removing the flask from the heat, allowing the precipitate to settle and examining the clear solution. A faint yellow color will appear as soon as the excess of barium has been precipitated and a few drops of the chromate in excess are present in the solution. The value of the chromate being equivalent to the barium chloride cc. per cc., the difference between the two titrations is due to the barium chloride required by the sulphate.

One cc. N/4 $BaCl_2$ = 0.01 gram SO_3.

NOTES. Salts of the alkalies, alkaline earths (Sr and Ca) and zinc and cadmium do not interfere. Nickel, cobalt and copper, however, give colored solutions which prevent the yellow chromate being seen. Should the latter be present, the end-point may be recognized by using ammoniacal lead acetate as an outside indicator (1 vol. NH_4OH + 4 vols. $PbC_2H_3O_2 \cdot 3H_2O$, 5% sol.), the indicator and titrated solution being mixed drop per drop on a white tile. A yellowish red color indicates the presence of chromate.

Precipitation of the Sulphate with Barium Chromate and Titration of Equivalent, Liberated Chromate with Iodine and Thiosulphate, Hinman's Method.[1]

The sulphate, precipitated by barium chromate, liberates an equivalent amount of chromic acid, which is determined by treating with potassium iodide and titrating the liberated iodine with thiosulphate.

Reactions. $Na_2SO_4 + BaCrO_4 = BaSO_4 + Na_2CrO_4$,

$Na_2CrO_4 + 3KI + 8HCl = 2NaCl + 3KCl + CrCl_3 + 4H_2O + 3I$,

$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

Procedure.[2] The solution of the sulphate, containing not over 2 per cent of SO_3, if acid, is almost neutralized with potassium hydroxide, then heated to boiling, and an excess of barium chromate solution added.[3] After boiling for one to five minutes, the hot solution is neutralized by adding calcium carbonate[4] until no further effervescence occurs. The precipitate is filtered off and washed with hot water. The combined filtrates containing the chromate liberated by the sulphate through double decomposition, is acidified with 5 cc. strong

[1] Treadwell and Hall, "Analytical Chemistry," **2**, 3d Ed., p. 716. Pennock and Morton, J. Am. Chem. Soc., 2265, 1903.

[2] Hinman, Am. Sci. and Arts, **3**, 478, 1877.

[3] The barium chromate used should be free from soluble chromate, barium carbonate or soluble barium salt. The compound may be prepared by precipitating with potassium chromate added to a boiling solution of barium chloride. The precipitate is washed with boiling water containing a little acetic acid, and finally with pure water, and then dried. Four grams of the dry salt are dissolved in a liter of normal hydrochloric acid.

[4] In presence of iron, zinc and nickel, the solution is neutralized with ammonium hydroxide and an excess added; after boiling, the solution is filtered. By using calcium carbonate insoluble basic chromates of these elements would be formed, and low results for SO_3 would follow. This is avoided by the use of ammonia.

hydrochloric acid per each 100 cc. of filtrate and an excess of potassium iodide added. Iodine equivalent to the chromic acid is liberated. This is titrated with N/10 sodium thiosulphate.

One cc. of N/10 thiosulphate = 0.003269 gram H_2SO_4.[1]

Benzidine Hydrochloride Method [2]

Benzidine sulphate, $C_{12}H_8(NH_2)_2 \cdot H_2SO_4$, is scarcely soluble in water containing hydrochloric acid. The weak base benzidine is neutral to phenolphthalein and the acid in its sulphate may be titrated with an alkali.[3] The method gives reliable results in the analysis of all sulphates, provided no substances are present which attack benzidine, and provided the amount of other acids and salts present is not too great.[3]

Reaction. $Na_2SO_4 + C_{12}H_8(NH_2)_2 \cdot 2HCl = 2NaCl + C_{12}H_8(NH_2)_2 \cdot H_2SO_4$ and

$C_{12}H_8(NH_2)_2 \cdot H_2SO_4 + 2NaOH = C_{12}H_8(NH_2)_2 \cdot 2H_2O + Na_2SO_4$.

Reagent. *Benzidine hydrochloride* is prepared by taking 6.7 grams of the free base, or the corresponding amount of the hydrochloride and mixing into a paste with 20 cc. of water in a mortar. Twenty cc. of hydrochloric acid (sp.gr. 1.12) are added and the mixture diluted to exactly 1000 cc. One cc. of this solution corresponds to 0.00357 gram H_2SO_4. The solution has a brown color. Brown flakes are likely to separate out on standing, but these do no harm.

Procedure. The sulphate solution is diluted with water so that there is at least a 50-cc. volume for each 0.1 gram sulphuric acid present. An equal volume of the reagent is vigorously stirred in, and the precipitate allowed to settle for ten minutes. The solution is filtered onto a double filter, placed on a porcelain, perforated plate in a funnel (a Büchner is O.K.), gentle suction being applied. The last portions of the precipitate are transferred to the filter by means of small portions of the clear filtrate, and the compound then washed with 20 cc. of cold water added in small portions and sucked dry with each addition. The precipitate and filter are placed in an Erlenmeyer flask, 50 cc. of water added, and the mixture shaken until homogeneous. Phenolphthalein indicator is now added, the mixture heated to about 50° C. and titrated with N/10 sodium hydroxide. When the end-point is nearly reached, the liquid is boiled for five minutes, and the titration then completed.

One cc. N/10 = 0.004904 gram H_2SO_4.

[1] N/10 $Na_2S_2O_3 = \frac{H_2SO_4}{30} = 98.08 \div 30 = 3.269$.

[2] Method suggested by Raschig, Z. a. Chem., 617 and 818, 1903.

[3] Friedheim and Nydegger (Z. a. Chem., **9**, 1907) have found that there should not be more than 10 mol. HCl, 15 mol. HNO_3, 20 mol. $HC_2H_3O_2$, 5 mol. alkali salt, or 2 mol. ferric iron present to 1 mol. H_2SO_4.

DETERMINATION OF PERSULPHATES

Ferrous Sulphate Method

Ferrous salts in cold solutions are oxidized to ferric form by persulphates. Advantage is taken of this action in the quantitative determination of persulphates.

Reaction. $2FeSO_4+H_2S_2O_8=Fe_2(SO_4)_3+H_2SO_4$.

Procedure.[1] About 2.5 grams of the persulphate are dissolved in water and diluted to 100 cc. Ten cc. of this solution, equivalent to one-tenth of the sample, weighed out, are placed in a flask and a considerable excess of standard ferrous sulphate solution [2] added, say 100 cc. measured out from a burette. The solution is diluted with an equal volume of hot, distilled water (70 to 80° C.), and the excess ferrous sulphate titrated with N/10 potassium permanganate. This titration is deducted from the permanganate equivalent of 100 cc. of the ferrous solution taken (if this amount was used). The difference is due to persulphate oxidation.

One cc. N/10 $KMnO_4=0.009708$ gram $H_2S_2O_8$; or $=0.0114$ gram $(NH_4)_2S_2O_8$; or $=0.01352$ gram $K_2S_2O_8$.

Oxalic Acid Method [3]

Oxalic acid, in presence of silver sulphate, reduces persulphates in accordance with the reaction,

$$H_2C_2O_4+H_2S_2O_8=2H_2SO_4+2CO_2.$$

Procedure. About 0.5 gram of the persulphate is placed in an Erlenmeyer flask, 50 cc. of N/10 oxalic acid added, together with 0.2 gram silver sulphate in 20 cc. of 10% sulphuric acid solution. The mixture is heated on the water bath until the evolution of carbon dioxide ceases (about twenty minutes). The liquid is diluted to 100 cc. with warm water and titrated warm (about 40° C.) with N/10 potassium permanganate. The excess of oxalic acid is titrated, the difference is due to oxidation by the persulphate.

For calculation see factors in previous method.

[1] Method suggested by Le Blanc and Eckardt, C. N., **81**, 38.

[2] About 30 grams of ferrous sulphate or ferrous ammonium sulphate crystals are dissolved in 900 cc. of water and the volume made to 1000 cc. with concentrated sulphuric acid. The reagent is standardized against N/10 potassium permanganate and the value per cc. in terms of the standard permanganate noted, the cc. permanganate solution required divided by the cc. of ferrous sulphate solution taken for titration, gives value of the reagent in terms of the permanganate.

The solutions are best verified upon a persulphate of known purity.

[3] R. Kempf, Ber., **38**, 3965, 1905.

DETERMINATION OF SULPHUR IN COMBINATION AS SULPHIDES, SULPHITES, BISULPHITES, METABISULPHITES, THIOSULPHATES, SULPHATES.

Available Hydrogen Sulphide in Materials High in Sulphide Sulphur. Iron Sulphide, Sodium Sulphide, etc.

Evolution Method. Since it is desired to obtain the H_2S that ordinarily would be obtained when the sulphide is treated with a strong acid, the mat of metallic aluminum or zinc and the addition of stannous chloride solution used in the procedure given on page 401 is omitted here.

Procedure. 0.5 to 1 gram of the sulphide is placed in the dry evolution flask. All connections are now made as directed in the general procedure. Three absorption bulbs containing neutral solution of cadmium sulphate are connected to the condenser, and supported by wires attached to the thistle tube and the arm of the condenser. All connections being tight, 100 cc. of dilute sulphuric acid, 1 : 4 are added through the thistle tube and H_2S evolved. The procedure is now the same as described on page 401.

Titration. When the evolution of the H_2S is complete, the bulbs containing the precipitate are emptied into a beaker and carefully washed out. The precipitate is now filtered and washed five or six times until free of acid. Methyl orange is added to the filtrate and the free acid titrated with N/10 NaOH.

The precipitate may be titrated with iodine according to (*b*) under general method of procedure, using an excess of iodine, followed by starch and acid and then titrating back with sodium thiosulphate solution. A double check may thus be obtained. See page 402.

If it is desired to weigh the CdS precipitate, it is best to evolve the H_2S into a neutral solution of cadmium salt. The precipitate formed in a neutral or slightly acid solution is crystalline and easily filtered, whereas that formed in an ammoniacal solution is gelatinous.

When a neutral $CdSO_4$ or $CdCl_2$ solution is used, H_2S should be evolved by sulphuric acid and not by hydrochloric acid, as the latter is volatile, and will pass through the condensing bulb recommended in the general procedure.

One cc. N/10 NaOH = .001704 gram H_2S
" " = .004396 gram FeS
" " = .003904 gram Na_2S.

Hydrogen Sulphide and Soluble Sulphides

Direct titration of hydrogen sulphide water, and soluble sulphides in solution may be made in absence of other substances acted upon by iodine. The solution containing the sulphide is added to an excess of N/10 iodine solution, made acid with hydrochloric acid, and the excess iodine titrated with N/10 sodium thiosulphate. The following reaction takes place:

$H_2S+I_2=2HI+S$. The cc. $Na_2S_2O_3$ are subtracted from cc. I = I reacting with H_2S. One cc. N/10 iodine = 0.00174 gram H_2S.

NOTE. The soluble sulphide may be determined gravimetrically by oxidizing with bromine, the reagent being added until the solution is colored brownish red, the excess of the halogen removed by boiling and the sulphate precipitated as $BaSO_4$.

Determination of a Sulphide and a Sulphydrate in Presence of Each Other

When a mixture of sulphide and sulphydrate is treated with iodine the following reactions take place:

$$H_2S+I_2=2HI+S \quad \text{and} \quad NaHS+2I_2=NaI+HI+S.$$

It will be noticed that the acidity produced by the first reaction is twice that caused by the iodine action on the sulphydrate, and that the acidity in the latter titration remains unaffected. The reactions with the alkali salts is effected by addition of a standard iodine solution containing a known amount of hydrochloric acid. The reactions in this case are as follows:

$Na_2S+2HCl=2NaCl+H_2S$ and $NaSH+HCl=NaCl+H_2S$. The iodine reacts with the H_2S as follows: $H_2S+I_2=2HI+S$.

From the second set of reactions it is evident that the quantity of hydriodic acid formed by the action of iodine on the sulphide is equivalent to the hydrochloric acid required to decompose the sulphide, so that the acidity remains unchanged. On the other hand with sulphydrate, NaSH, the hydriodic acid formed by the iodine oxidation, is twice the equivalent of hydrochloric acid required to decompose the acid salt. Hence it is evident that the acidity is a measure of the quantity of sulphydrate present in the mixture. From the second set of reactions the following procedure is devised.

Procedure. To a measured amount of N/10 iodine solution containing a measured amount of N/10 hydrochloric acid (the mixture diluted to 400 cc.) is added the solution containing the sulphide and sulphydrate from a burette, until the stirred solution becomes a pale yellow color. (The cc. of solution added is noted and its equivalent of the sample calculated.) Starch is now added and the excess of the iodine titrated with N/10 sodium thiosulphate. The cc. of thiosulphate in terms of N/10 solution subtracted from the cc. N/10 iodine solution taken give cc. iodine required by the sample added. The acidity of the solution is now determined by titration with N/10 sodium hydroxide. The cc. NaOH required by the HI give total NaOH minus cc. N/10 HCl present in the iodine solution.

Calculation. *A*. Cc. N/10 iodine required by the sample minus twice the cc. of N/10 NaOH required by HI formed by the reaction multiplied by 0.003903 give weight of Na_2S, (i.e., cc. I -2 cc. NaOH) $\times 0.003904$ = gram Na_2S.

B. Cc. N/10 NaOH required by the HI multiplied by 0.00560 gives gram weight of NaHS. Or in brief: cc. NaOH $\times 0.005608$ = gram NaHS.

The above weights multiplied by 100 and divided by the weight of sample used in the iodine titration give per cent of constituents in the sample.

The method is of value in the analysis of alkali sulphides in absence of other compounds, which are decomposed by hydrochloric acid and which react with iodine.

Determination of Thiosulphate in Presence of Sulphide and Sulphydrate

The sulphide and sulphydrate sulphur is removed from the solution by adding an excess of freshly precipitated cadmium carbonate. The solution is filtered and diluted to a definite volume and the thiosulphate determined on an aliquot

portion by running it into an excess of N/10 iodine solution and titrating the excess of iodine with N/10 thiosulphate solution.

One cc. N/10 iodine = 0.024822 gram $Na_2S_2O_3 \cdot 5H_2O$.

Determination of Sulphates and Sulphides in Presence of One Another

In one portion of the sample the sulphide is decomposed and the hydrogen sulphide expelled by boiling the solution (in presence of CO_2 replacing air in the flask) after acidifying with hydrochloric acid. The sulphate sulphur may now be precipitated as $BaSO_4$ by the usual methods.

In a second portion total sulphur is determined after oxidizing the sulphide with an excess of bromine and boiling out the excess of halogen. Total sulphur minus sulphate sulphur = sulphide sulphur.

The sulphide may be oxidized with fuming nitric acid by boiling the solution in a flask with reflux condenser. The nitric acid is expelled by evaporating the solution down to a moist residue. The sulphate is now precipitated by taking up the residue with water, adding HCl and then sufficient $BaCl_2$ to cause complete precipitation.

Determining the Sulphur in Thiocyanic (Sulphocyanic) Acid and its Salts

Oxidation of the sulphur may be accomplished as described for sulphides in the preceding method either by means of bromine or by fuming nitric acid. The sulphur is then precipitated as $BaSO_4$ as usual.

Determination of Sulphurous Acid (SO_2 in Solution) Free, or Combined in Sulphites, Acid Sulphites, Metabisulphites and Thiosulphates

Gravimetric Method, Oxidation to Sulphate and Precipitation as $BaSO_4$. Sulphur dioxide, free or combined in a soluble salt, may be oxidized to SO_3 or sulphate by means of an oxidizing agent such as chlorine, or bromine, or hydrogen peroxide (alkaline solution). The sulphuric acid or sulphate may be then precipitated and determined as $BaSO_4$ in the usual way.

Procedure. The halogen (bromine preferred) is added (in a water-saturated solution) in large excess to the sample, the free halogen then boiled out, and sulphuric acid precipitated, from a solution made slightly acid with hydrochloric acid, by addition of a solution of barium chloride, according to the standard procedure.

If hydrogen peroxide is used, the solution should be made alkaline with ammonia and the peroxide added, the excess boiled out, and the solution then made acid as directed above.

$BaSO_4 \times 0.3517 = H_2SO_3$, or $\times 0.5401 = Na_2SO_3$, or $\times 0.4458 = NaHSO_3$, or $\times 0.3387 = Na_2S_2O_5$, or $\times 0.2745 = SO_2$.

NOTE. If hydrogen peroxide is used, it should be tested for H_2SO_4 and allowance made accordingly.

Volumetric Methods

Titration with Iodine. Sulphurous Acid, Sulphites, Metabisulphites, Thiosulphates. Sulphurous acid, combined or free, may be titrated with iodine solution, the following reaction taking place:

$$SO_2+2I+2H_2O=H_2SO_4+2HI.$$

The titration is accomplished by adding the solution of sulphurous acid, sulphite, or thiosulphate to the iodine, not in the reverse order, since in the latter order low results are obtained, unless the solution is very dilute (less than 0.04% SO_2).[1]

Procedure. Five grams of the sample (sulphurous acid solution titrated directly) are dissolved in a little water and transferred to a 500-cc. graduated flask, then made to volume. Each cc. of this solution contains 0.01 gram of the sample; 100 cc. of N/10 iodine, or their equivalent if the solution is stronger or weaker, are placed in a beaker together with a few drops of hydrochloric acid. A portion of the sample in a 100-cc. burette is now run into the iodine, with constant stirring, until the color of the free iodine has almost faded out; a little starch solution is now added and the titration continued to the complete fading of the blue color.

Since each cc. of the sample contains 0.01 gram of the material, it follows that the 100-cc. iodine equivalent in terms of the material titrated expressed to the fourth decimal place as a whole number, if divided by the cc. of the sample required, will give the per cent of the substance sought, provided other titratable substances are absent.

Example. Suppose *sodium sulphite* is being titrated, then since 100 cc. of N/10 iodine are equivalent to 0.6304 gram Na_2SO_3, 6304 divided by the cc. Na_2SO_3 solution required gives per cent Na_2SO_3. If 63 cc. were required the salt would be 100% pure.

NOTE. When the iodine equivalent is over unity, it is necessary to take a larger sample per 500-cc. volume to avoid having a titration of over 100 cc. For example in the *analysis of sodium thiosulphate*, a 20-gram sample is diluted to 500 cc. and a portion of this added to 100 cc. of N/10 iodine solution. In this case it must be kept in mind that each cc. of the sample contains 0.04 gram of thiosulphate and the percentage calculated accordingly upon completing the titration.

If the titration of the iodine is made in a casserole, the end-point may readily be recognized without the addition of starch.

Equivalents. 100 cc. N/10 iodine solution will oxidize:

Sodium sulphite (anhydrous), $Na_2SO_3=0.6304$ gram, or 0.3203 gram SO_2.

Sodium sulphite, $Na_2SO_3.7H_2O=1.2606$ grams.

Acid sodium sulphite, $NaHSO_3=0.5204$ gram.

Sodium metabisulphite, $Na_2S_2O_5$ (anhydride of $NaHSO_3$) $=0.47535$ gram.

Sodium thiosulphate, $Na_2S_2O_3\cdot5H_2O=2.4822$ grams.

NOTE. Hydrogen sulphide or sodium sulphide are also titrated with iodine. Equivalents for 100 cc. N/10 iodine $=0.1704$ gram H_2S, or 0.3904 gram Na_2S.

[1] A secondary reaction takes place, the hydriodic acid formed reducing the SO_2 to S, e.g., $SO_2+4HI=2H_2O+2I_2+S$. (J. Volhard, Ann. d. Chem. u. Pharm., **242**, 94.) The solution, if not too dilute, will show a distinct separation of sulphur. (Treadwell and Hall, "Analytical Chemistry," **2**, 3d Ed.) Raschig believes that a loss of SO_2 occurs, due to evaporation. (Z. Angew. Chem., 580, 1904.) See Sutton, "Volumetric Analysis," 10th Ed., pp. 128, 129. Gooch, "Methods in Chemical Analysis," 1st Ed., pp. 364–368.

Determination of Sodium Thiosulphate. The iodine titration is described on page 410. See also the chapter on iodine.

Acidimetric and Alkalimetric Methods

Titration of Sulphites, Acid Sulphites (Metabisulphite) or Sulphurous Acid. The choice of indicator is important as the titration with one may be different from that obtained in presence of another. For example the titration of sulphurous acid by an alkali in presence of phenolphthalein is twice the titration necessary to obtain an alkaline reaction with methyl orange. The reason for this is evident by the fact that Na_2SO_3 is neutral to phenolphthalein and alkaline to methyl orange, whereas $NaHSO_3$ is neutral to methyl orange but is acid to phenolphthalein. Advantage is taken of this in the analysis of salts containing a mixture of the normal and acid salts.

Reaction. With phenolphthalein $H_2SO_3+2NaOH=Na_2SO_3+2H_2O$.

With methyl orange $H_2SO_3+NaOH=NaHSO_3+H_2O$.

On the other hand if a salt is being titrated, methyl orange cannot be used for the titration of metabisulphite or acid sulphite, since these salts are neutral to this indicator, here phenolphthalein is required and an alkali titration made.

Reaction. $NaHSO_3+NaOH=Na_2SO_3$. ($Na_2S_2O_5+H_2O=2NaHSO_3$.)

Again if sodium sulphite, Na_2SO_3, is to be titrated, phenolphthalein would not do as an indicator, since Na_2SO_3 is neutral to this indicator. Here an acid titration is required with methyl orange indicator present:

$$2Na_2SO_3+H_2SO_4=2NaHSO_3+Na_2SO_4.$$

A. Sulphurous Acid

For the alkali titration of this acid it is advisable to use methyl orange as indicator, since this is not affected by carbon dioxide, which is very frequently present.

Reaction. $H_2SO_3+NaOH=NaHSO_3$.

One cc. N/1 NaOH = 0.06407 gram SO_2, or = 0.08209 gram H_2SO_3.

B. Sodium Metabisulphite

Sodium acid sulphite does not exist in dry form, since the salt loses water and the anhydride $Na_2S_2O_5$ results. This is analogous to sulphurous acid, which exists only in water solution. It has been found that the acid sulphite solution evaporated to crystallization yields a product, which though dried with extreme care, forms the anhydride salt, $Na_2S_2O_5$. For correct report, therefore, the solid should be reported as metabisulphite, and the solution of the salt as acid sulphite.

Since metabisulphite in solution, or acid sulphite, is neutral to methyl orange, phenolphthalein indicator must be used and an alkali titration made. Carbon dioxide-free water and reagents should be used.

Reaction. $Na_2S_2O_5+H_2O=2NaHSO_3$ and $NaHSO_3+NaOH=Na_2SO_3+H_2O$.

Procedure. 9.507 grams of the finely ground powder are dissolved in about 50 cc. of cold saturated salt solution, to which has been added from a burette 50 cc. of normal sodium hydroxide. The salt solution should be made neutral to

phenolphthalein. One cc. of 0.1% solution of the indicator is added and the excess acid sodium sulphite titrated with normal sodium hydroxide until a permanent faint pink color is obtained.

Since the normal equivalent of the salt has been taken for analysis the cc. alkali titration, including the 50 cc. originally present, will give the percentage directly in terms of $Na_2S_2O_3$.

NOTE. The NaCl serves to give a sharp and more permanent end-point. It may be necessary to add more of the indicator towards the end of the titration.

C. Sodium Sulphite, Na_2SO_3

Sodium sulphite, Na_2SO_3, is neutral to phenolphthalein and alkaline to methyl orange. The titration of this salt is accomplished by addition of standard acid in presence of methyl orange.

Reaction. $2Na_2SO_3+H_2SO_4=Na_2SO_4+2NaHSO_3$.

Procedure. The normal factor weight (12.6 grams) of the salt is dissolved in about 250 cc. of distilled water, 1 cc. of methyl orange added, followed by normal sulphuric acid, added from a burette until a faint orange end-point is obtained. As in the case of the metabisulphite, each cc. of normal sulphuric acid equals 1% Na_2SO_3. Hence the percentage is obtained directly from the burette reading.

NOTES. Organic chlorine matter may be removed from the solution by filtering through charcoal.

If sodium carbonate is present, it will also be titrated. A correction must be applied for this. In the presence of sodium carbonate the solution will be alkaline to phenolphthalein. An approximate estimation of this may be obtained by titration with normal acid in presence of this indicator, remembering that sodium bicarbonate, $NaHCO_3$, is neutral to phenolphthalein, hence twice this titration must be deducted from the total methyl orange titration, i.e., $Na_2CO_3+H_2SO_4$ (M.O.) = $Na_2SO_4+H_2CO_3$ and $2Na_2SO_3+H_2SO_4$ (P.) = $2NaHSO_4+2NaHCO_3$. (Alkaline hydroxides will also be titrated.) CO_2 may also be obtained by the standard procedure under carbon, the SO_2 being oxidized by addition of chromic acid. $Na_2CO_3\times1.5$ = equivalent Na_2SO_3.

Sodium carbonate may be detected in a sulphite or metabisulphite by adding cold, dilute acetic acid (25%) to the dry powdered salt. An effervescence is due to the presence of carbonate, since a sulphite or metabisulphite does not effervesce under similar conditions.

Determination of Sulphites, Metabisulphites, Thiosulphates, Sulphates, Chlorides and Carbonates in Presence of One Another

1. Sodium Sulphite, Na_2SO_3

This is determined by titration with standard acid in the presence of methyl orange indicator according to the standard procedure previously described. If a carbonate is present, allowance must be made for this as stated

One cc. N/1 H_2SO_4 = 0.126 gram Na_2SO_3. *Calculate to per cent.*

$Na_2CO_3\times1.5$ = equivalent Na_2SO_3.

2. Sodium Metabisulphite, $Na_2S_2O_5$

This is determined by titration with a standard alkali in the presence of phenolphthalein indicator according to the procedure previously described.

One cc. N/1 NaOH = 0.09507 gram $Na_2S_2O_5$. *Calculate to per cent.*

3. Sodium Thiosulphate, $Na_2S_2O_3$

One gram of the mixed salts is placed in 100 cc. of N/10 iodine solution, and the excess of iodine titrated with N/10 sodium thiosulphate according to the standard procedure.

Calculation. $\{(\text{cc. N/10 I} - \text{cc. N/10 } Na_2S_2O_3) - [(\%\ Na_2S_2O_5 \times 2.104) + (\%\ Na_2SO_3 \times 1.5864)]\} \times 1.5814 = \%\ Na_2S_2O_3$.

4. Sodium Sulphate

The sample is dissolved in a little water, hydrochloric acid added, and the solution boiled to expel all of the SO_2. Barium sulphate is now precipitated and determined according to the standard procedure.

$$BaSO_4 \times 0.6086 = Na_2SO_4.$$

NOTE. The amount of the sample required is governed by the per cent Na_2SO_4 present.

5. Sodium Chloride

The sample is dissolved in water, nitric acid added and the solution boiled until all the SO_2 has either been volatilized or oxidized. The chlorine of the chloride is now precipitated with silver nitrate from a hot solution by the usual procedure.

$$AgCl \times 0.4078 = NaCl.$$

NOTE. The amount of the sample taken is governed by the per cent of NaCl present.

6. Sodium Carbonate, Na_2CO_3

Carbon dioxide is evolved from the mixture by means of chromic and sulphuric acids, the former being used to oxidize the SO_2 of the sample. The evolved gas is bubbled through a mixture of strong sulphuric and chromic acids to remove any SO_2 that may have escaped oxidation. Fig. 20. The CO_2 is absorbed either in caustic and weighed or is passed into a standard solution of barium hydroxide and titrated according to the standard procedures given under carbon.

NOTE. The amount of the sample taken is governed by the per cent of Na_2CO_3 present.

DETERMINATION OF FREE SULPHUR IN A MIXTURE

From 1 to 10 grams of the material, depending upon the amount of sulphur present, is extracted in a Soxhlet extractor (see modified form Fig. 61) with carbon tetrachloride, or carbon bisulphide (freshly distilled) for twelve hours. The extract is evaporated to dryness, adding 10 cc. of bromine-carbon tetrachloride mixture together with 15 cc. of nitric acid. The residue is taken up with 10 cc. of hydrochloric acid, diluted with 150 cc. of distilled water, heated to boiling and the sulphuric acid precipitated with 10% barium chloride solution, washed, dried, ignited and weighed according to the procedure for sulphur.

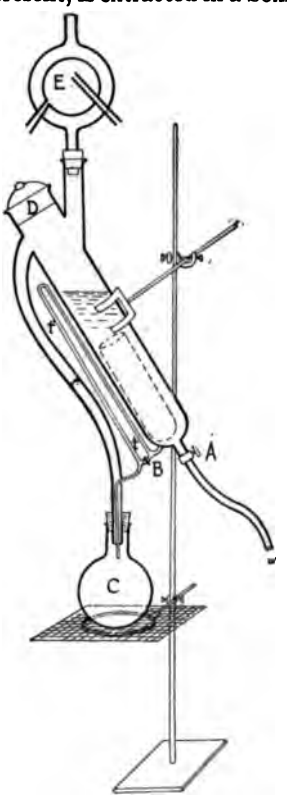


FIG. 66.—Sanders' Extraction Apparatus.

$$BaSO_4 \times 0.58851 = Ba.$$

$$\frac{BaSO_4 \times 100 \times 0.13738}{\text{Weight of sample}} = \text{per cent free sulphur.}$$

Sanders' extraction apparatus[1] has several advantages that make this apparatus desirable for laboratory use, where a number of daily extractions are required. As may be seen from Fig. 66, by simply removing the glass stopper *D* the cylinder may be charged without disconnecting the apparatus, as is necessary with the Soxhlet type of apparatus. The extraction is carried on with the traps *A* and *B* closed, the siphon *t-t'* acting automatically as in case of the Soxhlet. With *A* closed and *B* open the apparatus may be used as a reflux condenser. The solvent liquid may be drawn off by opening *A*. With *B* closed and *A* open the apparatus may be used as a condenser and the ether, chloroform, carbon disulphide, etc., distilled from *C*. The globe-shaped Soxhlet condenser may be replaced by Allihn's or Liebig's condenser, if desired. The ball form, however, is more compact.

EVALUATION OF SPENT OXIDE FOR AVAILABLE SULPHUR

Spent oxide is the by-product of gas works, and refers to the spent Fe_2O_3 used in the scrubber for the removal of hydrogen sulphide from the gas. The FeS, as in case of pyrites, is used in the manufacture of sulphuric acid, and is evalued by its available sulphur content.

Total Sulphur. The oxide is sampled, brought into solution and the sulphur

[1] J. McC. Sanders, Proc. Chem. Soc., **26**, 227–228, 1910. The Analyst, **35**, 556, 1910.

etermined exactly as is given under the standard method for determination of ulphur in pyrites ore.

Residual Sulphur. Two grams of the material are ignited to expel volatile ulphur, a porcelain crucible being used. The residue is treated with strong ydrochloric acid and after digestion on the steam or water bath is diluted with vater and filtered. (If SiO_2 is present evaporation to dryness is necessary.) Sulphur is determined in the filtrate as usual.

Available Sulphur. The per cent of residual sulphur is subtracted from the per cent total sulphur, the difference being available sulphur.

Iron. This may be determined on an ignited sample according to a standard procedure for iron. See chapter on Iron.

ANALYSIS OF BRIMSTONE

The impurities in brimstone are seldom more than a few tenths per cent. In the usual analysis, moisture, available sulphur, ash, arsenic, and chlorine are required.

Moisture. The powdered sample, weighing 50 grams, is spread out on a watch-glass and dried for an hour at 100° C., then cooled in a desiccator and weighed.

Loss of weight in grams multiplied by 2 = per cent moisture.

Available Sulphur. Ten grams of the sulphur taken from the dried material are heated in a silica or porcelain dish until the sulphur ignites. The heating is discontinued during the burning of the substance, but renewed for a minute or so after the sulphur has burned away. Loss of weight of the cooled residue is due to the available sulphur.

NOTE. Organic matter in brimstone is not appreciable.

Ash. This is the residue that remains in the dish. The increase of weight of the tared dish is due to the ash.

Arsenic. Ten grams of the material are treated with 30 cc. of carbon tetrachloride mixture (3 parts CCl_4+2 parts Br) and after standing for ten minutes 25 cc. strong nitric acid are added in small portions (a watch-glass covering the beaker during the intervals of addition). The mixture is taken to dryness on the steam bath. Water is added and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit Method for arsenic.

NOTE. Arsenic-free reagents should be employed.

Chlorine. One hundred grams of the brimstone are extracted with hot water, the filtered extracts oxidized with 10 to 15 cc. of nitric acid and a few crystals of ammonium persulphate by boiling and treated with 5 cc. of 10% solution of silver nitrate. The solution, brought to boiling, is placed in a dark place and the silver chloride allowed to settle. This is now filtered off in a weighed Gooch crucible and chlorine calculated from the AgCl.

$$AgCl \times 0.2474 = Cl \text{ or } = 0.4078 = NaCl.$$

THORIUM

R. STUART OWENS [1]

Th, *at.wt.* 232.4; *sp.gr.* 7.7; 11.00; *m.p.* 1700°; *oxides* ThO_2.

DETECTION

(1) By means of the spectroscope. Thorium shows lines of greatest intensity in the arc spectrum at 4863.3, and 4919.9. In the spark spectrum lines of greatest intensity at 3221.4, 3300.6, 4382.1, 4391.1.

(2) By the addition of H_2O_2 to a neutral solution of the nitrates containing ammonium nitrate. See page 418.

(3) By radio activity. Thorium compounds possess the power of continually emitting Becquerel rays and radio active emanations.

ESTIMATION

The estimation of thorium is required chiefly in the fabrication of incandescent gas mantles. Raw materials such as monazite PO_4(Ca,La,Di,Th)) and thorite ($ThSiO_4$) are generally used. The former usually contains from 2 to 4% of thorium while the latter runs as high as 81.5%. Thorium nitrate in a rather impure state is the chief intermediate product. The finished mantles generally contain 99% ThO_2 and 1% CeO_2.

Preparation and Solution of the Sample

"A" Silicates (as thorite, etc.)[2] are decomposed by treatment with ten times their weight of fuming hydrochloric acid. This treatment usually suffices, but in cases where an insoluble residue still remains it is fused with ten times its weight of sodium carbonate in a large platinum crucible. The fusion is dissolved in hydrochloric acid and added to the solution obtained from the first extraction. After the silica and the metals of the first group are removed in the usual way the solution is freed from H_2S by boiling. The thorium together with the other rare earths, calcium, magnesium, etc., are then present as chlorides and the necessary separations made as detailed under gravimetric determination.

"B" Phosphates (as Monazite, etc.) (*1*) ***By Fusion with Potassium Acid Sulphate.***[3] 0.5 gram of the finely pulverized material is mixed with 10 grams of potassium acid sulphate in a large platinum crucible, covered and heated until gentle fusion takes place and no further gas is given off. Then ignite over free flame for a few minutes, cool and treat with a little water and hydrochloric acid, until complete decomposition takes place. Boil for a few minutes, allow to cool and settle and decant off the clear liquid. The residue is treated with concen-

[1] Research Chemist, New York City.
[2] Lunge, "Technical Methods of Analysis."
[3] Benz, "Zeit. für angew. Chem., p. 297, 1902.

trated hydrochloric acid. Dilute and filter from the residue of silicic and tantalic acids. The filtrate then contains the thorium, etc., as chlorides. Determinations are made as detailed under gravimetric methods following.

(2) ***By Sulphuric Acid Extraction.*** The finely pulverized sample is mixed with sufficient H_2SO_4 to form a paste and the mass heated gently at first, then gradually increasing the heat to low redness. After cooling the rare earths are dissolved from the mass with cold water. The thorium is then present in the solution as sulphate. After removal of the base metals in the usual way determinations are carried out as detailed below.

" C " Oxides (as gas mantles, etc.). In the case of gas mantles the organic matter is first burned off and the resulting oxides heated with three times their weight of strong H_2SO_4 in a porcelain casserole. The mixture is heated on the sand bath at a temperature slightly below that required to drive off fumes of SO_3 for a few minutes. After cooling the contents are diluted with a small quantity of water and allowed to stand for several hours. The sulphates completely dissolve and the sample is ready for the gravimetric estimation as detailed.

SEPARATIONS

(1) The hydroxide is insoluble in an excess of the precipitant.

(2) The sulphate forms double salts with K_2SO_4, which are insoluble in an excess of the reagent.

(3) Thorium oxalate readily forms a double oxalate with ammonium oxalate in an excess of the reagent.

(4) Thorium is precipitated together with the rare earths by oxalic acid.

(5) Thorium and cerium may be separated from all of the other earthy metals if the hydroxides recently precipitated are suspended in water containing 4 to 5 times their weight of caustic soda and a current of chlorine gas passed through the solution. All of the other metals dissolve. The insoluble residue left under these conditions is gelatinous like aluminum hydroxide.

(6) Thorium may be completely separated from cerium by precipitation with H_2O_2 from a neutral solution containing 10% of ammonium nitrate. The thorium being precipitated as the peroxide which on ignition readily changes to the oxide ThO_2.

GRAVIMETRIC METHOD FOR DETERMINING THORIUM

The solution of the chlorides or sulphates after being freed from the base metals, silica, etc., is made nearly neutral with ammonium hydroxide and the rare earths precipitated by the addition of oxalic acid in solution. In the case of monazite sands where 0.5 gram sample was used 1 gram of oxalic acid is generally sufficient, but in any case the precipitate should be allowed to settle and the clear solution tested by the further addition of oxalic acid. Allow to stand at least twenty-four hours, then filter and wash thoroughly with water. The precipitate is then washed into a casserole and treated with strong nitric acid, adding a little at a time until complete decomposition has taken place. Then evaporate to dryness on the steam bath to remove the excess acid. A second evaporation with water should follow in cases where the precipitate is appreciable. Take up

with 10% ammonium nitrate in sufficient quantity to cause a dilution of one part of thorium nitrate in 100 parts of water. Heat to 60°–80° C. and precipitate the thorium with 20 cc. of pure 3% H_2O_2 solution for each 100 cc. solution. The precipitate which is usually colored yellow by traces of cerium peroxide is filtered at once, washed with hot water containing ammonium nitrate. By reprecipitation after solution in nitric acid and neutralizing the excess acid with ammonia pure thorium peroxide may be obtained. The precipitate is ignited in a platinum crucible and weighed as ThO_2.

Thorium nitrate is assayed by precipitating the thorium as peroxide according to the details given above.

DETERMINATION OF MINUTE AMOUNTS OF THORIUM JOLLY'S METHOD[1]

Solids after pulverizing are fused with an alkali carbonate at 1000° C. and the fusion extracted with water. The residue is dissolved in dilute hydrochloric acid and set aside for some days in order to allow thorium disintegration products to develop. The thorium is then determined by boiling off the emanations in a constant stream of air which is passed through an electroscope. The rate of discharge of the electroscope is compared with that produced when a known amount of thorianite was tested. It is necessary to boil the solutions before testing to expel any radium emanation that may be present.

[1] J. S. C. I., 8, Vol. **24**, 422.

TIN

H. A. Baker[1] and B. S. Clark[2]

Sn, *at.wt.* 118.7; *sp.gr.* 6.56; *m.p.* 232°; *b.p.* 2275°; *oxides* SnO_2 *and* SnO.

DETECTION

Tin is separated, together with arsenic, antimony, gold and platinum, from the hydrogen sulphide precipitate of the metals of the second group, by the action of yellow ammonium sulphide. (Normal ammonium sulphide does not readily dissolve the sulphides of tin.) If the ammonium sulphide solution is acidulated with hydrochloric acid and the acid solution reduced with iron, antimony, arsenic, platinum and gold are precipitated in the metallic form. The presence of tin, which is present as stannous chloride, is indicated by the reducing action of the solution on mercuric chloride, a white precipitate of HgCl or a gray precipitate of Hg being thrown down.

Reduce the hydrochloric acid solution of the sample by means of a small piece of iron wire. Treat with an excess of cold potassium hydroxide. Filter if the solution is not clear. Add an ammoniacal solution of silver nitrate. (One part $AgNO_3$: 16 parts NH_4OH.) A brown precipitate of metallic silver indicates the presence of tin. Antimony, arsenic, platinum and gold are precipitated by the iron, while all of the heavy metals remaining, except lead, tin, aluminum, chromium, and zinc, are removed by the treatment with potassium hydrate.

Welch and Weber[3] recommend the following method for detection of tin: Add 10 cc. concentrated hydrochloric acid to the superficially dried precipitated sulphides from the ammonium sulphide separation. Filter off arsenic which does not decompose. Dilute filtrate to 70 cc. volume. Saturate with H_2S. Heat to expel excess H_2S. Add 5 cc. of hydrogen peroxide and heat until precipitate is redissolved. Add 5 to 10 grams of oxalic acid and pass H_2S into the hot solution. Antimony separates as a red sulphide. Filter. Filtrate contains the tin. Reduce with test lead and add mercuric chloride. White or grayish precipitate indicates presence of tin.

ESTIMATION

The estimation of tin is required in connection with the analysis of tin ores, dross, ashes, dust, tin plate, alloys such as solder, canned foods, and general analysis.

Opening Up Tin Ores

As the oxides of tin are not readily soluble in acids the tin can be most easily removed by assay. Ores, slags, dross, and ashes are first subjected to the assay process. The button obtained is then analyzed either volumetrically or gravi-

[1] Chief Chemist, American Can Company.
[2] First Assistant Chemist, American Can Company.
[3] Jour. Am. Chem. Soc., 38, 5, 1011, 1916.

metrically by one of the methods given below. Having the weight of the button and the per cent of tin in it, the per cent of tin in the sample as received can be calculated.

There are two general processes of assaying, namely, the Cyanide Process and the Carbonate of Soda Process.

The Cyanide Process

The theory of this method is that the oxides are reduced to the metal by the action of potassium cyanide, the reaction being represented as follows:

$$SnO_2 + 2KCN = Sn + 2KCNO.$$

Potassium cyanide reduces other metals also so that the button obtained is not pure.

Procedure. Take 100 grams of the sample which has been dried and finely powdered. (For complete analysis the moisture should be determined in the usual way.) Mix thoroughly with four times its weight of powdered potassium cyanide. Place about 1 in. of potassium cyanide in the bottom of a number H (height 5¾ ins., diameter 3¾ ins.) Battersea clay crucible. Place the mixture of sample and cyanide on top of the cyanide in the crucible and cover with enough more cyanide to fill the crucible to within 1 in. of the top.

Place the crucible in the assay furnace and heat slowly until it has been thoroughly warmed and the cyanide begins to melt. Then increase the heat gradually to a pure white, taking care that the cyanide does not boil over.[1] Grasp the crucible with the tongs and tap it gently on the hearth to assist in settling the metal. Continue the heating until all of the organic matter has disappeared, adding more cyanide from time to time if necessary. Near the end of the process the molten mass becomes clear and transparent and finally pasty and translucent. When this last condition appears, remove the crucible from the furnace and allow it to cool slowly at the temperature of the room.

When cool, break the crucible and slag away from the button. The appearance of the button and the slag immediately surrounding it indicates whether or not the process has been properly manipulated. The button itself should be firm and compact and the slag around it should be white or greenish in color. If the button is spongy or if the slag has a dirty black color, the assay should be discarded and a new determination made, using a fresh sample.[2]

Weight of Button = per cent Metal in Sample.

$$\frac{\text{Weight of Metal} \times \text{per cent Sn}}{100} = \text{per cent Sn in the Sample.}$$

NOTE. This process should be carried on under a hood in a segregated room, and every precaution should be taken to avoid breathing the poisonous fumes of potassium cyanide.

[1] Lunge advises that the cyanide should not be allowed to boil. He uses a small sample (10 grams). "Technical Methods of Chemical Analysis" 1, Part 1, p. 256. It is our experience that satisfactory results are not obtained unless the extreme heat of the furnace is used.

[2] See also Mellor, "A Treatise on Chemical Analysis," p. 270, 1913.

The Sodium Carbonate Method

The sample is fused with equal parts of sodium carbonate and sulphur.[1] The fusion is then dissolved in water. The tin goes into solution as a thiostannate of sodium. Iron and copper are then separated by the addition of sodium sulphite, leaving arsenic, antimony and tin in solution.[2]

Other Methods of Opening Tin Ores

Fusion with Sodium Hydrate. The sample of ore is fused with ten times its weight of sodium hydrate. The process is carried out in an iron crucible and then transferred to nickel. The fused mass is dissolved in water and the tin determined in the usual way.[3]

Reduction by Means of Hydrogen. The ore may be reduced by strongly igniting in a porcelain tube in a current of hydrogen. The reduced metal is then dissolved in hydrochloric acid and the tin estimated by a standard method.

Fusion with Sodium Peroxide. J. Darroch and C. Meiklejohn[4] opened ores, slags, etc., by fusing with sodium peroxide in a nickel crucible. They dissolve the fused mass in hot water and acidify with hydrochloric acid. The sample is then ready for the necessary separations.

SEPARATIONS

Tin is separated from iron, aluminum, chromium, etc., by the insolubility of its sulphide in dilute hydrochloric acid. Tin, together with antimony, arsenic, platinum and gold, is separated from lead, mercury, copper, cadmium and bismuth, by the solubility of its sulphide in yellow ammonium sulphide. Antimony, arsenic, platinum and gold are precipitated as metals from a hydrochloric acid solution by the action of metallic iron, leaving tin in solution.

A few special separations are of interest.

Tin and Lead. For the analysis of an alloy of lead and tin, it is usually preferable to make the estimations on different samples. In this case, lead is estimated by Thompson's method and the tin by Baker's modification of the iodine method. Lead can also be separated from tin by the method given below for the separation of tin and copper.

Tin and Copper. This alloy can be dissolved in concentrated hydrochloric acid by the addition of potassium chlorate. A large excess of ammonium tartrate is added and the solution made alkaline with ammonia. Copper is then precipitated as sulphide by the addition of hydrogen sulphide water until no more precipitate is formed.

[1] Very finely divided carbon is sometimes preferred. Air must not be allowed to enter the crucible. Else decomposition is not complete. Mellor, "A Treatise on Chemical Analysis," 1913, p 270. If carbon is used instead of sulphur the process becomes one of reduction to the metal and is carried out in the assay furnace. The details of operation are similar to the cyanide process. The metal separates as a button in the bottom of the crucible. The button contains other metals with the tin and must be analyzed further for exact percentages.

[2] Mellor objects to the method as being tedious and dirty.

[3] Low, "Technical Methods of Ore Analysis," 3d Ed., pp. 208–213, 1908.

[4] Engineering and Mining Journal, 81, 1177, 1906.

Tin and Antimony. Antimony is separated, in the metallic form, from the hydrochloric acid solution of the alloy, by the action of metallic iron placed in the solution. The tin may be determined by the iodine method without the removal of the antimony. If the antimony is desired, it may be filtered off and determined in the usual way.

As in the case of lead, it is usually quicker and more accurate to make these determinations on separate samples. The tin can be determined by the iodine method. The antimony can be determined volumetrically by various methods, preferably the bromate. (See chapter on Antimony.)

Tin and Phosphorus. One-half gram of the alloy is dissolved in 15 cc. of concentrated hydrochloric acid containing potassium chlorate. This is diluted to 200 cc. with water and warmed. It is then treated for a long time with hydrogen sulphide gas. The tin is all precipitated as sulphide while the phosphorus remains in solution.

Tin and Iron and Aluminum. Tin is separated from iron and aluminum by precipitation, as sulphide, from the hydrochloric acid solution.

Iron may also be separated from tin with copper, and lead by precipitation as sulphide from the alkaline ammonium tartrate solution.

Tin and Tungstic Acid. Donath and Mullner [1] separate tin oxide from tungstic acid by mixing the sample with zinc dust and strongly igniting in a covered crucible for fifteen minutes—boiling with dilute hydrochloric acid; oxidizing with potassium chlorate to change the blue tungstic oxide to tungstic acid and diluting with water. It is then allowed to stand overnight and filtered. The tin is in solution.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF TIN

Determination of Tin or the Oxides of Tin by Hydrolysis

This method depends upon the precipitation of meta-stannic acid in the presence of ammonium nitrate when the stannic chloride is diluted to considerable volume and heated to boiling. It is especially applicable to the determination of tin oxide in tin paste, but may be extended to all chloride solutions of the higher oxides. The reaction involved proceeds as follows:

$$SnCl_4+4NH_4NO_3+3H_2O$$

$$=H_2SnO_3+4NH_4Cl+4HNO_3.^2$$

Stannous tin may be determined by oxidizing the chloride solution to the stannic form. The method gives concordant results and is rapid.

Procedure. For the analysis of tin paste take a catch weight of about 10 grams for a sample. Dissolve this sample by heating it in a No. 6 beaker with 300 cc. of concentrated hydrochloric acid. Transfer the acid solution to a 500-cc. volumetric flask and make up to the mark with dilute (1 : 1) hydrochloric acid.

[1] J. Chem. Soc. Absts., **54**, 531, 1888.

[2] Fresenius, "Quantitative Chemical Analysis," **1**, 406, 1903. Sodium sulphate may be used instead of ammonium nitrate. In that case the reaction is

$$SnCl_4+4Na_2SO_4+3H_2O=H_2SnO_3+4NaCl+4NaHSO_4.$$

Take 50 cc. (approximately 1 gram) for a working sample. (If the determination is to be made on tin paste, the sample may be obtained directly by one of the methods described under Opening Tin Ores.) Dilute to 100 cc. with cold water. Nearly neutralize with strong ammonia and finish by adding drop by drop from a burette, dilute ammonia until a slight permanent precipitate is formed. A large amount of ammonia will tend to precipitate iron, if present, as a hydrate and to re-dissolve the meta-stannic acid.[1] Add 50 cc. of a saturated solution of ammonium nitrate. Dilute to 400 cc. with boiling water, stirring constantly. Bring the solution to an incipient boil, remove from the flame and allow the beaker to stand on the steam bath until the precipitate has settled.[2] The solution above the precipitate should be clear. Decant the supernatant liquor through a 12½ cm. S. & S. 590 filter paper and wash the precipitate by decantation[3] six times, using 200 cc. of boiling water and allowing the precipitate to settle thoroughly at each washing. Transfer the precipitate to the filter, "cop" out the beaker and wash down with hot water in the usual way. After the precipitate has been allowed to drain, transfer to a porcelain or a silica crucible and dry carefully on an asbestos board over a Bunsen flame.[4] When dry, ignite at a low temperature until the filter paper has been consumed. Increase the heat and finally blast to constant weight.

$$\frac{\text{Weight } SnO_2 \times 100 \times .7877}{\text{Weight of sample}} = \text{per cent Sn.}$$

Determination of Tin as Sulphide

The determination of tin as a sulphide involves many difficulties and should be avoided if possible. Better results can be obtained by the volumetric methods and in most cases without the necessity of preliminary separations of interfering metals. If tin must be separated as a sulphide, better results would be obtained if the precipitate were dissolved and the tin content determined by the iodine method.

Having the hydrochloric acid solution of tin after the interfering metals have been separated, to precipitate tin sulphide, neutralize with ammonia and then acidify with acetic acid. Pass hydrogen sulphide until the solution is saturated. Allow the precipitate to settle overnight. Pour the supernatant liquor off through a Gooch crucible and wash the precipitate six times by decantation, using a solution of ammonium nitrate[5] for wash water. Finally transfer to the crucible and wash free from chlorides. Dry the crucible in an oven at 100° C. Heat slowly in a Bunsen flame until[6] all the sulphur has been expelled. Care should be taken at this point to avoid forming fumes of stannic sulphide by heating too rapidly.

[1] Some practice is required to judge accurately the exact point when the necessary amount of ammonia has been added. The precipitate should appear white.

[2] If the boiling continues more than a few seconds the precipitate will not settle properly. Time will be saved in this case if the sample is discarded and a new determination commenced.

[3] If meta-stannic acid is washed over onto the filter at this point, clogging will result and a great deal of time will be lost.

[4] Spattering is likely to occur here, causing loss.

[5] Sulphide of tin separates as a slimy mass which tenaciously retains alkaline salts, especially in the absence of ammonium salts. Mellor, "Treatise on Chemical Analysis," p. 308, 1913.

[6] Bichloride of tin, Acker process, page 425.

Remove the lid of the crucible, which should be kept in place during the first part of the heating, and raise the temperature gradually, finally finishing with the blast. As sulphuric acid is usually present in some quantity, the crucible should be cooled and a small piece of ammonium carbonate should be placed in it. Repeat the ignition to drive out the acid. Cool and weigh as SnO_2.[1]

BICHLORIDE OF TIN

Bichloride of tin is of great importance in some of the industries, especially the textile. It is necessary to have exact analytical control of the processes in which this compound is used in order to insure uniform results and to certify the efficiency and economy of the process. Several methods have been developed for this purpose. The ones given below have had practical application and have proven to be satisfactory.

Stannic Acid Method.—Hot-water Precipitation. In the textile industry where bichloride of tin is used, the efficiency of the process depends directly on the neutrality of the tin liquor. If there is more than enough chlorine present in the bichloride solution to exactly oxidize all the tin to the stannic form, this excess is called "free HCl." If there is not enough chlorine present to do this, the deficiency is spoken of as "basic HCl." The difficulty of determining the "free" or "basic" HCl is apparent when it is known that $SnCl_4$ readily decomposes in water, liberating free acid. The following method has been developed especially for this purpose and has given good results.

The important point in this analysis is to determine whether the liquor has "free" HCl present or whether it is "basic" in nature. It has been found that hot water precipitates tin from the $SnCl_4$ solution as stannic hydroxide and at the same time liberates the chlorine as free HCl.

$$SnCl_4+4H_2O=Sn(OH)_4+4HCl.^2$$

The $Sn(OH)_4$ separates in a colloidal precipitate which may be filtered off and the tin estimated as SnO_2. The liberated acid may be determined in the filtrate, and from this data the "free" or "basic" HCl can be calculated.

Procedure. For accurate work about 20 grams of the liquor should be weighed out in a tared weighing bottle, but for works control, where time is an important factor, it is sufficiently accurate to get the specific gravity of the liquor by means of a hydrometer and take a measured quantity for a sample, calculating the weight from these data.

Transfer the sample to a 100-cc. volumetric flask. Make up to volume with cold distilled water. Draw out of this solution 10 cc. (approximately 2 grams) and place in a 150-cc. tall beaker. Fill the beaker nearly full with boiling hot water, stirring continuously while the water is being poured in.[3] Place the beaker on top of the steam bath and allow the precipitate to settle. Decant the liquor

[1] This method is generally used only when minute traces of tin are present, and then it is considered best to dissolve the sulphide in hydrochloric acid and make the final determination by the iodine method. (See analysis of Canned Foods for "Salts of Tin," page 430.)

[2] Holleman and Cooper, "Text Book of Inorganic Chemistry," 4th Ed., 1912.

[3] If the solution is not stirred at this point, the precipitate will not settle and trouble will be experienced during the filtering process.

rough an 11 cm. 590 S. & S. filter [1] and wash the precipitate six times by decantaon, using hot water. Now transfer the precipitate to the filter and continue he washing until 1 drop of the filtrate gives no test for chlorine. After most of he water has drained out of the filter, place the paper and precipitate in a tared ilica crucible. If there is plenty of time, dry the contents of the crucible on an sbestos board over a low Bunsen flame. In case the analysis must be made in , hurry, cover the crucible [2] and heat it very carefully over a low flame until all he water has been driven out and the paper has been charred. Then remove he cover and increase the heat to the full Bunsen flame and finally blast to contant weight. Weigh as SnO_2. Titrate the filtrate with N/1 NaOH, using methyl range as the indicator.

Calculation:

$$SnO_2 \times .7877 = Sn$$

$$Sn \times 2.1945 = SnCl_4$$

$$SnCl_4 - Sn = \text{Cl equiv. to Sn}$$

$$Cl \times 1.0282 = \text{HCl equiv. to Sn}$$

$$\frac{\text{HCl}}{\text{Weight of sample}} = \text{per cent HCl equiv. to Sn}$$

$$\frac{\text{cc. N/1 NaOH} \times .03646}{\text{Weight of sample}} = \text{per cent HCl (actual).}$$

The difference between these last two figures equals " free " or " basic " HCl.

The Acker Process Method. [3] The theory of this method is practically the same as that of the hot-water method, except that in this case the liberated acid is neutralized with ammonia before the stannic hydroxide has been filtered off, the advantage being that any solution of the stannic hydroxide, by either acid or alkali, is prevented. The method is not applicable for the determination of " free " or " basic " HCl.

Procedure. Weigh out 25 cc. of the bichloride of tin solution. Transfer to a 500-cc. flask (volumetric) and make up to volume with cold water. With a standardized pipette, transfer 25 cc. of this solution to a No. 4 beaker. Dilute with hot water to precipitate most of the tin as stannic hydrate. Add 10 drops of phenolacetolin [4] (1 gram of phenolacetolin dissolved in 200 cc. of water). Titrate very carefully with dilute ammonia until the appearance of a rose-red color. Boil a few minutes on the hot plate. Allow the tin precipitate to settle. Decant through an 11-cm. filter paper (S. & S. 589, black ribbon brand). Wash rapidly with hot water without allowing the precipitate to cake down in the filter until the washings are free from chlorine. Dry the precipitate in an oven at 100° C. When dry, invert the filter into a tared porcelain crucible and heat on a gauze until the paper has disappeared. Remove the gauze and heat with the full

[1] Time may be saved by using a platinum cone with the filter and applying a gentle vacuum. This can be done with very little danger of breaking the paper.

[2] This precaution must be taken, else there will be a loss by decrepitation.

[3] Kindness of W. F. Dorflinger, chief chemist of Perry-Austin Manufacturing Company.

[4] Luteol may be used as indicator, giving a yellow color at the end-point. It is slightly more delicate but much more expensive.

Bunsen flame for a few minutes. Finally blast to constant weight.[1] Weigh as SnO_2.

Take the filtrate and washings and dilute them to a volume of 1000 cc. Warm 500 cc. of this solution and saturate it with hydrogen sulphide. If any tin separates, filter and ignite in a tared porcelain crucible. Moisten with a little nitric acid and heat very slowly to drive out the acid. Ignite to constant weight. Weigh as SnO_2. Add this result to the SnO_2 obtained above when calculating the final result.

Determination of Tin in Bichloride of Tin as Sulphide

This method is given as an alternative for the Acker Process Method and may be used as a check on that process. Uniform and concordant results have been obtained by the use of the two methods.[2]

Procedure. Weigh out 25 cc. of bichloride and dilute to 500-cc. volume with cold distilled water. Take 25-cc. portions of this solution for analysis. Dilute the sample to 250 cc. Saturate with hydrogen sulphide. Warm the mixture on a hot plate at a temperature of about 65° C. until the precipitate is coagulated. Test the clear supernatant liquor for unprecipitated tin by adding a little hydrogen sulphide water. Filter on an ashless filter and wash free from chlorides. Make the filtrate and washings up to 1000 cc. volume for further determinations. Dry the tin sulphide precipitate on the filter in an oven at 100° C. Remove the precipitate from the paper as completely as possible. Ignite the paper in a weighed porcelain crucible. Cool and add a few drops of nitric acid. Repeat the ignition, heating very carefully at first until the acid has nearly all been driven out. Now place the main tin precipitate in the crucible. Cover, heat gently for a few minutes, moisten with fuming nitric acid, ignite very carefully for one-half hour and then blast for fifteen minutes. Weigh as SnO_2.[3]

VOLUMETRIC DETERMINATION OF TIN

Volumetric methods for the determination of tin are based upon the reducing power of stannous compounds. They vary according to the oxidizing agent used and the details of manipulation.

Lenssen's Iodine Method as Modified by Baker.[4] This method is a modification of Lenssen's Iodine Method for the determination of tin in alkaline solutions. It is especially applicable to the determination of "salts of tin" in canned foods and to the estimation of tin coating on tin plate, but is accurate, rapid and very satisfactory for alloys and general analysis.

The method is based on the action of iodine in the presence of stannous chloride in hydrochloric acid solution. The reaction involved is:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI.$$

[1] If there has been any reduction, a few drops of nitric acid may be added and the ignition repeated, heating slowly at first to prevent loss by decrepitation.

[2] W. F. Dorflinger, Perry-Austin Manufacturing Company.

[3] Pure ammonium carbonate may be added at the end to drive off the sulphuric acid more rapidly.

[4] The details of this method as given were developed by Mr. H. A. Baker at this laboratory and have been modified in accordance with the findings of several years of experience.

Iron, lead and antimony do not interfere with the reaction. Copper in small quantities does not interfere with the determination, but if it is present in large quantities as a salt, it is likely to produce low results. Determinations made by the writer[1] show that results are accurate when less than 10% of copper, as copper chloride, is present. Larger amounts gave consistently low results. The reason for this fact centers around the difficulty of reducing all the copper to the cuprous form. If any $CuCl_2$ is left in the solution, it reacts with the potassium iodide of the iodine solution, causing the precipitation of CuI and the liberation of free iodine.

$$CuCl_2+2KI=CuI+2KCl+I.$$

Copper present as the metal is not easily soluble or goes into solution in the reduced form and is not likely to disturb the determination.[2]

Solutions—Standard Tin Solution. Dissolve 5.79 grams of Kahlbaum's C. P. tin in C. P. hydrochloric acid. The solution of the tin is effected by placing about 150 cc. HCl in an Erlenmeyer flask, together with the tin, and boiling. After the tin has all been dissolved, transfer to a volumetric liter flask and make up to the mark with dilute hydrochloric acid.

1 cc. = .00579 gram Sn.

Standard Iodine Solution. Dissolve 12.7 grams of C. P. iodine in a water solution of 20 grams of potassium iodide. Make up to one liter and standardize against the standard tin solution. For tin plate analysis, it is convenient to adjust the iodine solution so that 1 cc. equals exactly .00579 gram of tin. Then, if a sample of the plate having a total surface of 8 sq.ins. is taken, 1 cc. of the iodine solution is the equivalent of one-tenth of a pound per base box.

Indicator. Dissolve 5 grams of pure soluble starch in 1 liter of water.

Air-free Water. Dissolve 12 grams of bicarbonate of soda in 1 liter of water. Add 20 cc. HCl and allow the resulting gas to escape. Keep in a stoppered bottle.[3]

Procedure. For practical purposes, take a sample, such that the tin content will be between .2 gram and .5 gram. A larger sample should be taken for extreme accuracy in order to decrease the possible technical error. Place the sample in flask *A* of the Sellars apparatus, Fig. 68, together with 100 cc. of conc. C. P. HCl. Stopper the flask and connect tubes *B* and *D*, as shown in the illustration. Boil until the metal is all dissolved. This point is indicated by the cessation of the hydrogen evolution and the appearance of large well-developed bubbles. If a sufficient amount of metallic iron is present in the sample, complete reduction is assured. If no iron was present in the sample, or if there was not enough to reduce all of the tin, make sure that the tin is all converted to the stannous form by adding aluminum foil (about 1 gram). Replace the stopper and connect as originally. Boil until normal bubbles reappear. Open cock *B* to allow CO_2[4] gas to enter. Place the flask in cooling bath *F* without disconnecting the apparatus. After the solution has become thoroughly

[1] Mr. B. S. Clark.

[2] Sulphates must not be present. They tend to have an oxidizing effect and spoil the results.

[3] There should always be an excess of bicarbonate of soda present in order that carbon dioxide will be generated during the washing process, thus preventing air from entering the flask at any time during the analysis.

[4] Carbon dioxide generated in a Kipp apparatus is likely to contain oxygen. It is much better to use liquid CO_2 such as can be purchased in the open market.

cool, disconnect tubes B^1 and D^1 from the splash bulbs. Wash the bulbs with "air free" water, allowing the washings to drain into the bulk of the sample. Remove the stopper and wash down the sides of the flask. About 50 cc. of water should be used in the washing so that the final sample contains about 25% HCl. Add 5 cc. starch solution and titrate with the standard iodine solution.

$$\frac{\text{cc. iodine} \times .00579 \times 100}{\text{Weight of Sample}} = \text{per cent Sn,}$$

or

$$\frac{\text{cc. iodine}}{10} = \text{pounds per "base box."}^2$$

The Sellars Apparatus. This apparatus is a device designed by Mr. W. S. Sellars of this laboratory for the purpose of facilitating the solution of tin samples out of contact with air. Added to this advantage, it is equipped with a water

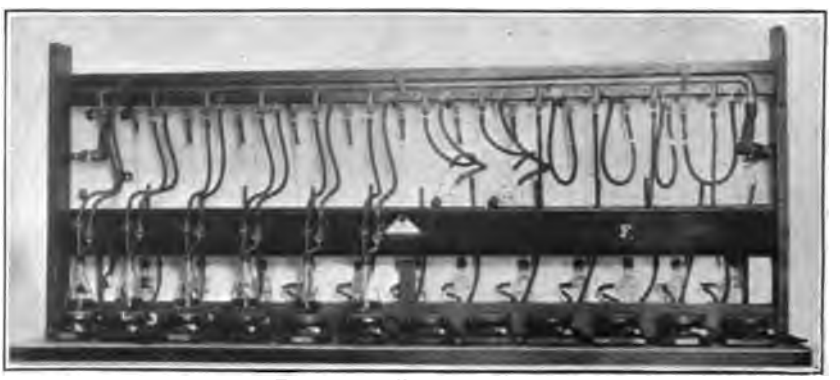


FIG. 67.—Sellars' Apparatus.

cooler. It is also constructed so that the tubes and scrubbing bottles can be cleaned by flushing with water. The use of this apparatus practically eliminates the usual sources of error in connection with the iodine method, and at the same time greatly increases the speed of the determination. Fig. 67 shows the apparatus in operation.

A.[1] 300-cc. Erlenmeyer flask.
B.[1] Connection with reduced pressure line from liquid carbon dioxide cylinder.
C.[1] Glass manifold.
D.[1] Exit connection to trap.
E.[1] Water trap to prevent escape of HCl fumes and to prevent air from backing into the flask.
F.[1] Cooling tank.
G.[1] Low-pressure water wash-out manifold.
H.[1] Perforated feed pipe to water cooler.
K.[1] Outlet for cooler.
L.[1] Electric hot plate.
M.[1] Lead drain pipe.

[1] See Fig. 68, page 429.
[2] "Basebox"—112 sheets of tin, 14×20 ins.

ɛrric Chloride Method.[1] This method depends upon the reduction of ferric ide by stannous chloride in hot solution.

$$SnCl_2+2FeCl_3=SnCl_4+2FeCl_2.$$

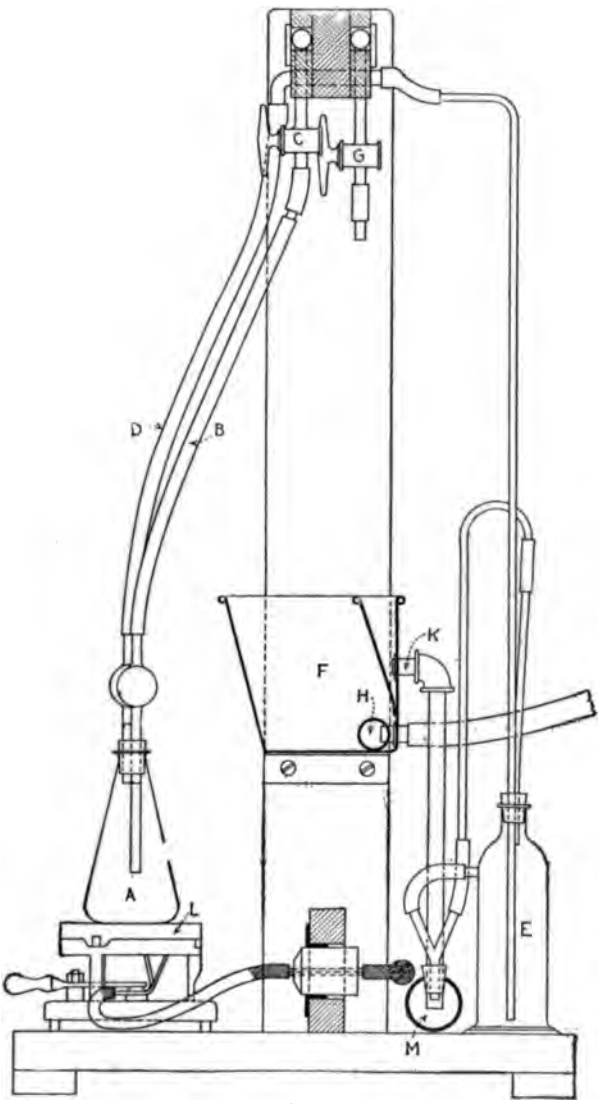


FIG. 68.—Sellars' Apparatus.

[1] C. Mene, **Dinglers Journal**, **117**, 230, 1850. K. Pallet and A. Allart, Bul. Soc. m. (2) 27, 43, 438, 1877. H. J. B. Rawlins, Chem. News, **107**, 53, 1913. H. smann, Zeit. Anal. Chem., **16**, 50, 1877.

Antimony, copper, arsenic, bismuth, mercuric chloride, tungsten and titanium must be absent.[1]

The Standard Solution of Ferric Chloride is made by dissolving pure iron wire in hydrochloric acid. To standardize this solution, dissolve 1 gram of pure tin in 200 cc. of C. P. HCl, preventing air from coming in contact with the solution by means of a trap, or by passing carbon dioxide over it.[2] Titrate this standard sample with the ferric chloride solution. The end-point is indicated by the yellow color, due to a slight excess of the iron solution.

Procedure. Tin is first separated from the interfering metals in the usual way. If lead, copper, arsenic, antimony or bismuth are present, the sample is first reduced, in the hydrochloric solution, with iron wire. The solution is then filtered. Lead and tin remain in the filtrate. Neutralize by adding strips of zinc until the action ceases. Tin and lead are precipitated. The clear liquid should show no trace of tin with hydrogen sulphide. Allow the precipitate to settle and wash by decantation, keeping the precipitated metals in the flask. Add 150 cc. of concentrated hydrochloric acid, keeping the contents of the flask protected from the air, and bring to a boil. When everything is dissolved, titrate to a yellow color with the ferric chloride solution.[3] This part of the analysis should be done very quickly to prevent oxidation by the oxygen of the air.

ELECTROLYTIC DETERMINATION OF TIN

Henz and Classen's Method. Results with this method at this laboratory have not been satisfactory.

Procedure. The tin is obtained as sulphide, dissolved in sodium sulphide solution and acidified with dilute acetic acid. It is then heated to boiling, and a boiling solution of equal parts of ammonium oxalate and oxalic acid added. The amount of this solution added should be such that the final mixture will contain thirty-five parts of oxalate and oxalic acid to one part tin. Use a current of .2 to .3 amp. having a voltage of two to three volts. After six hours add more oxalic acid and continue the electrolysis for another twenty-four hours.

ESTIMATION OF TIN IN CANNED FOOD PRODUCTS[4]

The tin in the canned food products is obtained as a sulphide precipitate from wet combustion, with nitric and sulphuric acids, of 100 grams food product.

The clear sulphuric acid residue is diluted, neutralized with ammonia and then rendered about 2% acid with hydrochloric acid, after which it is thoroughly saturated with hydrogen sulphide gas. This precipitate is then filtered on a Gooch crucible with a false bottom. The precipitate may contain foreign substances, such as lime, phosphorus, and silica, some lead, or even small amounts of

[1] Lunge, "Technical Methods of Chemical Analysis," 2, Part I, p. 267.

[2] The Sellars apparatus can be used with advantage for this purpose.

[3] The end-point can be easily identified by looking at a blue Bunsen flame through the solution. When a small quantity of ferric chloride is present, the flame appears green. Mellor, "A Treatise on Chemical Analysis," p. 310, 1913.

[4] H. A. Baker, Eighth International Congress of Applied Chemistry.

iron, but none of these will cause any trouble subsequently in the titration, so that the labor of separating the tin completely from the precipitate is obviated.

After washing the precipitate three or four times in a Gooch crucible, it is transferred to a small porcelain dish by simply forcing out the false bottom of the Gooch crucible and its asbestos pad and rinsing off the crucible.

The precipitate, mixed with asbestos, is now transferred to a 300-cc. Erlenmeyer flask and boiled with strong hydrochloric acid, potassium chlorate being added from time to time to insure the complete breaking up and solution of the tin sulphide, as well as the elimination of the sulphur. This is accomplished in a very few minutes. A few strips of pure aluminum foil, free from tin, are then added to the flask until all of the chlorine is eliminated. The flask is then attached to the Sellars apparatus and the determination completed, according to the details given under the Iodine Method.

Gravimetric Method.[1] The sample is first digested to a colorless or pale yellow solution as described under Baker's method.

Add 200 cc. water to the digested solution and pour into a 600-cc. beaker. Rinse out the Kjeldahl flask with three portions of boiling water so that the total volume of the solution is about 400 cc. Allow to cool and add 100 cc. concentrated ammonia. This amount of ammonia should render the solution nearly neutral, unless more than 50 cc. sulphuric acid have been used for digestion. The solution should be tested to see that it is still somewhat acid. In case of a large excess acid, add ammonia until just alkaline and then make about 2% acid with hydrochloric or sulphuric acid. Pass in a slow stream of hydrogen sulphide for an hour, having the covered beakers on an electric hot plate at about 95° temperature. Allow to digest on the hot plate for an hour or two.

Filter the tin sulphide on an 11-cm. filter. Wash with three portions of wash solution alternated with three portions of hot water. The wash solution is made up of 100 cc. saturated ammonium acetate, 50 cc. glacial acetic acid, and 850 cc. water. The filter papers used in this method are C. S. & S. No. 590, white ribbon.

Place the filter and precipitate in a 50-cc. beaker and digest with three successive portions of ammonium polysulphide, bringing to a boil each time and filtering through a 9-cm. filter. Wash with hot water. Acidify with acetic acid, digest on the hot plate for an hour and filter through a double 11-cm. filter. Wash with two portions of wash solution alternated with hot water and dry thoroughly in a weighed porcelain crucible. Thorough drying is essential to the success of the determination. Ignite very gently at first and later at full heat of Bunsen flame. Finally heat strongly with large burner, or Méker burner, having the crucible partly covered. Stannic sulphide must be gently roasted to the oxide, but the oxide may be heated strongly without loss, due to volatilization.

Weigh the stannic acid and convert to metallic tin by the factor .7877.

[1] E. L. P. Treuthardt, Association of Official Agricultural Chemists, August 15, 1915.

TITANIUM

WILFRED W. SCOTT and L. E. BARTON [1]

Ti, *at.wt.* 48.1; *sp.gr.* 4.5 [2]; *m.p.* 1795° C. (±15°)[3]; *oxides* TiO, Ti_2O_3, TiO_2, TiO_3.

DETECTION

The powdered ore is fused with potassium bisulphate, $KHSO_4$, until effervescence ceases. The cooled mass is dissolved in dilute sulphuric acid by boiling. ***Hydrogen peroxide,*** H_2O_2, added to this titanium solution, produces a yellow to orange color, according to the amount of titanium present. Hydrofluoric acid, or fluorides, destroys the color. Vanadium also produces this color with hydrogen peroxide, but the color is not destroyed by HF. The yellow color, according to Weller [4] is due to TiO_3 formed.

Morphine produces a crimson color with solutions of titanium in sulphuric acid.

Zinc added to hydrochloric acid solutions of titanium produces a blue color,[5] tin a fine violet solution.[6]

If ***sulphur dioxide,*** SO_2, is passed into the solution of titanium to reduce the iron, and the slightly acid solution then boiled, yellowish white metatitanic acid, $TiO(OH)_2$, is precipitated.

Bead Test on Charcoal. A small portion of the powdered mineral heated on charcoal with microscosmic salt and tin produces a violet-colored bead if titanium is present.

ESTIMATION

The element is widely distributed in minerals, soils, clays and titaniferous iron, $FeTiO_3$. It is found in granite, gneiss, mica, slate, syenitic rocks, granular limestone, dolomite, quartz, feldspars and a large number of other minerals. The principal commercial minerals are:

Ilmenite, $FeTiO_3$, containing about 52.7% TiO_2.
Rutile, TiO_2, containing 90 to 100% TiO_2.
Titanite, $CaTiSiO_5$, containing 34 to 42% TiO_2.
Perovskite, $CaTiO_3$, containing about 60% TiO_2 and 5 to 6% Yt_2O_3.
Titaniferous ores of variable titanic oxide content.

By far the most important application of titanium at the present time is the use of ferrotitanium in the iron and steel industry. The function of the titanium

[1] Chief Chemist Titanium Alloy Manufacturing Co.
[2] Hunter, Eighth Int. Congress Applied Chem., **2**, 125.
[3] Burgess and Waltenburg, U. S. Bureau of Standards.
[4] J. S. C. I., 1882, 506-508.
[5] Deville, C. N., **4**, 241.
[6] Cahen and Wootton, "The Mineralogy of the Rarer Metals."

is to deoxidize the steel and consequently to yield a product free from blowholes and segregation of impurities. In a steel thus purified the natural strength and resistant properties of the material are developed in the highest degree.

Next in importance is the application of titanium compounds to the textile industry. For use as a mordant in dyeing, the alkali titanium salts of organic acids, especially potassium titanium oxalate, have found extensive application. The use of titanous chloride and titanous sulphate for bleaching or discharging colors is increasing. Such bleaching agents are particularly applicable for silk and wool, which are injured by the action of those bleaching agents in which chlorine is the active element. Titanium compounds have also attained considerable importance in the dyeing of leather.

Titanium compounds are also used for electric light filaments, arc carbons, ceramics, fine brown glazes, paint for iron and steel, etc.

Preparation and Solution of the Sample

A knowledge of the solubility of the element and its oxides is of value in the solution of the sample.

Element. This is feebly soluble in cold dilute hydrochloric, or sulphuric acids; more readily so when the acids are heated. It is soluble in cold, concentrated hydrochloric acid; readily soluble in hot, concentrated hydrochloric, or sulphuric acids. It is scarcely acted upon by nitric acid, but readily dissolves in hydrofluoric acid. It is soluble by fusion with the alkalies.

Oxides. Ti_2O_3 is soluble in concentrated hydrochloric or sulphuric acids; forming, in the latter case, a violet-colored solution.[1] The oxide is insoluble in water and in ammonium hydroxide.

TiO_2 is difficultly soluble in concentrated sulphuric acid, less soluble if strongly ignited. The metatitanic acid, $TiO(OH)_2$, requires strong hydrochloric or sulphuric acid to effect solution, the orthotitanic acid, $Ti(OH)_4$, however, is readily soluble in hot or cold, dilute and concentrated acids. From titanic solutions orthotitanic acid is precipitated by ammonia, the precipitation being assisted by warming. Boiling a slightly acid solution precipitates the metatitanic acid, $TiO(OH)_2$. TiO_2 is soluble upon fusing with alkalies. TiO_2 is soluble in hydrofluoric acid, forming TiF_4, which is volatile, unless an excess of sulphuric acid is present (distinction from silica). The ignited oxide is best dissolved by fusion with $KHSO_4$ and heating the fused mass with dilute sulphuric acid solution. Titanous oxides have a black or blue color.

Salts. Many titanic salts are decomposed in the presence of water, precipitating titanic acid, the extent of the decomposition depending on the quantity of water used. Titanic sulphate is readily soluble in water and the solution is remarkably stable unless largely diluted with water. Some of the double salts are readily soluble and their solutions stable, i.e., potassium titanium oxalate.

General Considerations

Solution of Steel. The sample may be dissolved in hydrochloric acid (1 : 2). If a residue remains it is treated with a mixture of equal parts of hydrofluoric and sulphuric acids and a few drops of nitric acid, in a platinum

[1] Ebelmen, A. Ch., (3), **20**, 392, 1847.

dish, and the mixture evaporated to sulphuric anhydride fumes and to complete expulsion of hydrofluoric acid. The colorimetric procedure is now used for estimating titanium. For determination of titanium in hydrochloric acid solution see page 443.

NOTE. Titanium in steel treated with ferro carbon-titanium exists in two conditions: (1) Titanium soluble in hydrochloric acid. (2) Titanium insoluble in hydrochloric acid. Of the very small amount of titanium in treated steel the greater part will usually be found in the second form. When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble, and it is then occasionally desirable to determine also that existing in the second form.

Alloys. These are dissolved in concentrated nitric acid, aqua regia or a mixture of the dilute acids. Should nitric acid be used, the excess is expelled by evaporation to dryness with hydrochloric acid. The metals of the hydrogen sulphide group are removed in an acid solution by precipitation with H_2S, and titanium determined colorimetrically in the filtrate.

Ores. One to 5 grams of the ore are treated with 10 to 50 cc. of a mixture of sulphuric and hydrofluoric acids (1 to 5), a few drops HNO_3 added, and the solution evaporated to fumes to expel HF. If a residue remains upon taking up with water containing a little sulphuric acid, it is filtered off and fused with $KHSO_4$ as directed under the fusion method.

Fusion Method for Ores. The finely powdered sample is fused with four to five times its weight of potassium bisulphate, $KHSO_4$, and the cooled fusion dissolved with dilute sulphuric or hydrochloric acid. In the presence of silica potassium fluoride is added to assist in the decomposition of the material.

(See Analysis of Titaniferous Ores, page 445.)

Titaniferous Slags. One-half gram of the finely ground sample is decomposed in a platinum dish by a mixture of 5 cc. water, 5 cc. concentrated sulphuric acid, 2 cc. nitric acid, and 10 cc. of hydrofluoric acid, the reagents being added in the order named. The solution is evaporated rapidly to SO_3 fumes to expel fluorides and the excess sulphuric acid until residue is left nearly dry. After cooling it is taken up with 40 cc. of dilute hydrochloric acid (1 : 3), which will give a clear solution containing all the constituents of the slag except silica, which has been volatilized as SiF_4. The solution is diluted to 200 cc. with cold water. Iron and titanium are precipitated by ammonia in slight excess and filtered at once without boiling. The precipitate is dissolved in cold dilute hydrochloric acid and reprecipitated with ammonia. Titanium is now separated from iron by reducing iron with SO_2 and precipitating titanium from a boiling acid solution as described on page 436.

SEPARATIONS

Details of the isolation of titanium are given in the methods for its estimation.

Separation of Titanium from the Alkaline Earths, etc. The hydroxide is precipitated when a titanium solution containing ammonium chloride is treated with ammonium sulphide, whereas barium, strontium, calcium and magnesium remain in solution. Titanium hydroxide may be precipitated by making the solution containing titanium slightly ammoniacal with HN_4OH.

Separation from Copper, Zinc, Aluminum Iron, etc. Titanium is pre-

cipitated from a slightly acid solution [1] by boiling, passing sulphur dioxide through the solution to keep the iron reduced and prevent its precipitation.

Separation from the Bivalent Metals, Manganese, Nickel, Cobalt, Zinc. Titanium is precipitated along with aluminum and iron by hydrolysis of its acetate in a hot, dilute solution, whereas manganese, nickel, cobalt and zinc remain in solution. Details of the basic acetate method are given on page 260.

Separation of Titanium from Aluminum. Small amounts of titanium from large amounts of aluminum. (One part Ti to 50 parts Al.) Cupferron, $C_6H_5(NO)N\cdot ONH_4$ added to a decidedly acid solution containing titanium and aluminum precipitates titanium, but not aluminum. The precipitate is washed by decantation and then on the filter with very dilute hydrochloric acid to remove traces of aluminum. The procedure affords a separation of titanium from chromium, nickel, cobalt, manganese, etc. Copper and iron, however, precipitate with the titanium, if present in the solution. The yellow titanium salt has the composition $(C_6H_5(NO)NO)_4Ti$.[2]

Separation of Titanium from Iron. See Gravimetric Method for Determination of Titanium, Modified Gooch Method, below.

GRAVIMETRIC METHODS

Gravimetric Determination of Titanium. Modified Gooch Method [3]

This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron and from aluminum and phosphoric acid with which it commonly occurs. The procedure as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton has been found by the author [4] to give reliable results. The details of the method with a few slight changes found to be advantageous are given below. Iron is separated from titanium by precipitation as a sulphide in presence of tartaric acid, the organic acid is destroyed by oxidation and titanium precipitated from a boiling acetic acid solution. In the presence of alumina and phosphoric acid the impure precipitate is fused with Na_2CO_3 and the impurities leached out with boiling water. In presence of zirconium, titanic acid is incompletely precipitated. Hillebrand's modification for the removal of zirconium is given in the notes.

Procedure. Preparation of the Sample. ***Ores High in Silica.*** These may be decomposed by taking to SO_3 fumes with a mixture of 10 to 15 cc. of 50% hydrofluoric acid, HF, and 3 to 4 cc. of concentrated sulphuric acid per gram of sample.

Oxides. Decomposed by fusion with sodium or potassium bisulphate. The fusion is dissolved in 10% sulphuric acid, keeping the volume as small as possible. The sample should contain not over 0.2 gram titanium.

Precipitation of Iron. To the solution containing titanium, tartaric acid, equal to three times the weight of the oxides to be held in solution, is added. This should

[1] Acidity exactly 0.5% is best according to Levy, C.N., **56**, 209.
[2] Analyst, **36**, 520, 1912, method of J. Bellucci and L. Grassi.
[3] F. A. Gooch, Proc. Am. Acad. Arts and Sci., New Series, **12**, 435. Wm. M. Thornton, C. N., **107**, 2781, 123, 1913.
[4] W. W. Scott.

not exceed 1 gram of the organic acid, as the subsequent removal of larger amounts would be troublesome. H_2S is passed into the solution to reduce the iron and NH_4OH added to slight alkalinity followed by a further treatment with H_2S to completely precipitate FeS. The solution should be faintly alkaline (litmus) otherwise more ammonia should be added. After filtration and washing of the ferrous sulphide with very dilute and colorless ammonium sulphide, the titanium is entirely in the iron-free filtrate.

Oxidation of Tartaric Acid. Since titanium cannot be precipitated by any reagent in the presence of tartaric acid, the organic acid is oxidized by addition of 15 to 20 cc. of concentrated sulphuric acid to the sample placed in a 500-cc. Kjeldahl flask. The solution is evaporated to incipient charring of the tartaric acid. After cooling slightly, about 10 cc. of fuming nitric acid are added cautiously, a few drops at a time, and when the violent reaction has subsided the flask is heated gradually (hood), a vigorous reaction taking place accompanied by much effervescence and foaming with evolution of copious brown fumes. The organic matter gradually disappears, the effervescence becomes steady and finally ceases and white fumes of SO_3 are given off. The solution is cooled and the pale yellow syrup poured into 100 cc. of cold water, the flask washed out, adding the rinsing to the main solution. If cloudy, the solution is filtered.

Precipitation. Ammonia is added until the solution is nearly neutral, a point where the solution is slightly turbid, the precipitate dissolving upon vigorous stirring. If a trace of iron is suspected about 1 cc. of 10% ammonium bisulphate is added. Five cc. of glacial acetic acid followed by 15 grams of ammonium acetate or its equivalent in solution is added and the volume of the solution made up to about 350 cc. The solution is brought rapidly to boiling and maintained in ebullition for about three minutes. The titanium will precipitate in white flocculent and readily filterable condition. The precipitate is washed first with water containing acetic acid and finally with pure water. The filter and the precipitate are ignited cautiously over a low flame and finally blasted over a Méker blast for twenty minutes. The residue is weighed as TiO_2.

In the presence of large amounts of alumina and phosphoric acid, the residue above obtained is fused with sodium carbonate in a platinum dish and the fusion leached by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts and titanium oxide remains insoluble in the residue.

Ignited insoluble residue $= TiO_2$.

NOTE. Titanium may be separated from aluminum by fusing the residue with potassium acid sulphate, $KHSO_4$, and precipitation of titanium in an acid solution by cupferron. Al_2O_3 is in solution.

Determination of Titanium in Ferro Carbon Titanium. Gravimetric Method [1]

Into a 6-in. porcelain evaporating dish, weigh 0.6 gram (factor weight) of alloy.

Dissolve in a mixture of 15 cc. of dilute sulphuric acid (one acid to one water), 5 cc. of nitric acid, and 10 cc. of hydrochloric acid. Evaporate to fumes of sulphuric anhydride.

[1] Methods of analysis used in the laboratories of the Titanium Alloy Manufacturing Company.

Cool and take up by boiling with 50 to 60 cc. of water and 5 to 10 cc. hydrochloric acid. Filter into a 500-cc. beaker and wash the residue with hot water and dilute hydrochloric acid.

In the filtrate precipitate iron and titanium by ammonia in slight excess. Filter without boiling and wash precipitate twice on filter with hot water.

Reject filtrate. Dissolve the precipitate in a very little dilute hydrochloric acid, washing the filter with hot water and collecting the solution and washings in the original beaker.

Nearly neutralize the solution with ammonia or ammonium carbonate; dilute to 300 cc.; saturate with sulphur dioxide gas, and boil until titanic acid is precipitated and the solution smells faintly of sulphur dioxide.

Filter and wash with hot water and dilute sulphurous acid.

Dry, ignite, and weigh as titanic oxide.

Since the factor weight of sample has been used, one milligram of titanic oxide is equal to 0.1% metallic titanium.

VOLUMETRIC METHODS

The Determination of Titanium by Reduction, Addition of Ferric Salt and Titration of Reduced Iron with Potassium Permanganate [1]

Principle. Titanic acid is reduced by means of zinc, an excess of ferric sulphate is added and the ferrous salt, formed by reduction by titanous salt, is titrated with standard permanganate. The method is more accurate than direct titration of the titanous salt with permanganate.

Reaction. $Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4$,

or $TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$.[2]

Preparation of the Sample

Procedure. One to 2 grams of the ore is decomposed by hydrofluoric and sulphuric acids or by fusion with potassium bisulphate or a combination of the two according to the methods already described. Members of the H_2S group, if present, may be removed by H_2S. If iron is present it may be determined by boiling off the H_2S in the filtrate containing Fe, Ti, etc., and allowance made in the titration for titanium. If other interfering elements are present in this filtrate, titanic acid may be precipitated by boiling the slightly acid solution (sulphurous acid) according to directions given in the gravimetric method. The washed oxide is dissolved in strong H_2SO_4 and diluted as directed below.

Reduction. The solution is washed into a 100-cc. flask and diluted with water so that it will contain 10% of sulphuric acid. This acid holds titanic acid in solution and at the same time is insufficient to oxidize the reduced titanium oxide. Sufficient zinc to cause complete reduction is added and a rubber stopper carrying a Bunsen valve tube and a thistle tube with glass stop-cock is inserted

[1] H. D. Newton, A. J. Sc. (4), **25**, 130. A. F. Gooch, "Methods in Chemical Analysis."

[2] T. R. Ball and G. McP. Smith, Jour. Am. Chem. Soc., **36**, 1838, 1914.

in the neck of the flask. The evolved hydrogen expels the air and reduces the titanic oxide to the titanous form. Iron if present is also reduced. Gentle heat is applied until the excess of zinc dissolves. The solution is cooled and an excess of ferric sulphate added through the thistle tube, followed immediately by cold distilled water until the flask is filled to the neck. The contents of the flask is poured into a No. 6 beaker containing 150 to 200 cc. of cold distilled water and the ferrous iron, formed by the reducing action of titanous salt, is titrated with N/10 $KMnO_4$ solution.

One cc. N/10 $KMnO_4$ = 0.00481 gram Ti, or 0.00801 gram TiO_2.

Volumetric Method by Reduction of Titanium and Titration with a Ferric Salt

The following volumetric method recommended by the Titanium Alloy Mfg. Co., is essentially that described by P. W. & E. B. Shimer, Proceedings of Eighth International Congress of Applied Chemistry, the method hereafter described differing principally in the form of reductor and also in a few details of operation.

Reagents. Standard ferric ammonium sulphate solution.

Dissolve 30 grams of ferric ammonium sulphate in 300 cc. water acidified with 10 cc. of sulphuric acid; add potassium permanganate drop by drop as long as the pink color disappears, to oxidize any ferrous to ferric iron; finally dilute the solution to 1 liter.

Standardize this solution in terms of iron. The iron value multiplied by 1.4329 gives the value in titanic oxide (TiO_2); and the iron value multiplied by 0.86046 gives the value of the solution in terms of metallic titanium.

Indicator. Saturated solution of potassium thiocyanate.

Reductor. As a reductor a 500-cc. dispensing burette is used. The internal dimensions of the burette are $1\frac{5}{8}$ by 22 ins.

The reductor is charged with 1200 grams of 20-mesh amalgamated zinc, making a column about 12 ins. high and having an interstice volume of about 135 cc. This form of reductor is connveient, and when used as hereafter described is adapted to maintaining hot solutions, which is essential for complete reduction of the titanium.

The reductor is connected to a liter flask for receiving the reduced titanium solution, through a three-hole rubber stopper which carries also an inlet tube for carbon dioxide supply, and outlet tube for connecting with the suction pump.

Procedure. Determination of Titanium in Ferro-Carbon Titanium. One-half gram of sample is dissolved in a 6-in. porcelain evaporating dish in a mixture of 10 cc. water, 10 cc. sulphuric acid, 5 cc. of hydrochloric acid, 5 cc. of nitric acid.

The solution is evaporated to fumes of sulphuric anhydride; taken up by boiling with 50 cc. water and 10 cc. of hydrochloric acid; filtered and washed with hot water and hydrochloric acid.

The filtrate and washings should be about 100 cc. in volume.

The reductor is prepared for use by first passing through it a little hot dilute sulphuric acid followed by hot water, finally leaving sufficient hot water in the reductor to fill to the upper level of the zinc.

The hot titanic solution prepared as described above is now introduced,

about 100 cc. of water being drawn from the reductor into the original beaker to bring the solution to about the upper level of the zinc. The water thus removed will not contain any titanium if the operation has been conducted as described; but it serves as a safeguard and is also *convenient* to acidify this water with 10 cc. of sulphuric and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

The titanium solution is allowed to remain in the reductor for ten minutes.

While the solution is being reduced the receiving flask is connected to the reductor and the air completely displaced by carbon dioxide, conveniently drawn from a cylinder of the liquefied gas.

When the reduction is complete the receiving flask is connected with the suction pump, and while still continuing the flow of carbon dioxide the reduced solution is drawn out, followed by the reserved acid wash and then three or four 100-cc. washes with hot water. The displacement of the sample solution and washing of the zinc is so regulated by means of the stop-cock that the reductor is always filled with solution or water to the upper level of the zinc.

When the washing is complete, gradually release the suction to prevent air being drawn back into the receiving flask.

Disconnect the flask, add 5 cc. of potassium thiocyanate solution as indicator and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced which will remain for at least one minute.

The method is also well adapted for determining titanium in other titanium products, suitable means being employed for bringing the titanium into sulphuric acid solution.

Colorimetric Determination of Titanium with Hydrogen Peroxide

Preliminary Considerations. Hydrogen peroxide added to acid solutions of titanium produces a yellow to orange color, the depth of the color depending upon the amount of titanium present. Upon this fact the method is based. It is of especial value in determining small amounts of titanium, as it is possible to detect less than one part of the metal per hundred thousand parts of solution. Color comparisons can best be made on samples containing 0.05 to 5 milligrams of the element; larger amounts produce too deep a color for accurate comparison.

The following interferences should be made note of, e.g., molybdenum, vanadium and chromium also produce a color that would lead to error. Iron if present to the extent of 4% or over produces a color that must be allowed for; e.g., 0.1 gram Fe_2O_3 in 100 cc. of solution is equivalent to about 0.2 gm. of TiO_2 oxidized by H_2O_2 in 100 cc. of solution. Fluorides destroy the color, hence must be absent.[1] Phosphoric acid and alkali sulphates have a slight fading action,[2] hence must be allowed for by adding equivalent amounts to the standard if they are present in the sample. The addition of an excess of sulphuric acid partly counteracts the action of phosphates or alkali sulphates.[3] The color intensity is increased by increase of temperature, hence the standard and the sample

[1] W. F. Hillebrand, J. A. C. S., **17**, 718, 1895. C. N., **72**, 158, 1895.
[2] P. Faber, Zeit. an. Chemie, **46**, 277, 1907.
[3] H. E. Merwin, A. J. S. (4), **28**, 119, 1909.

examined should have the same temperature.[1] Since metatitanic acid produces no color with hydrogen peroxide, its formation must be prevented; the presence of 5% of free H_2SO_4 accomplishes this.[2]

The procedure is very satisfactory for magnetic or other iron ores. It is fully as accurate as the best gravimetric method and very much more rapid.

Solutions Required. ***Standard Titanium Solution.*** This may be prepared by precipitations of TiO_2 from K_2TiF_6 according to the gravimetric procedure and purification by solution and reprecipitation, the fluorine being first removed by taking the compound to fumes with H_2SO_4 and then hydrolyzing titanium with NH_4OH. The washed precipitate is ignited over a Méker flame for fifteen minutes, cooled in a desiccator and placed in tightly stoppered bottle, since TiO_2 is slightly hydroscopic.

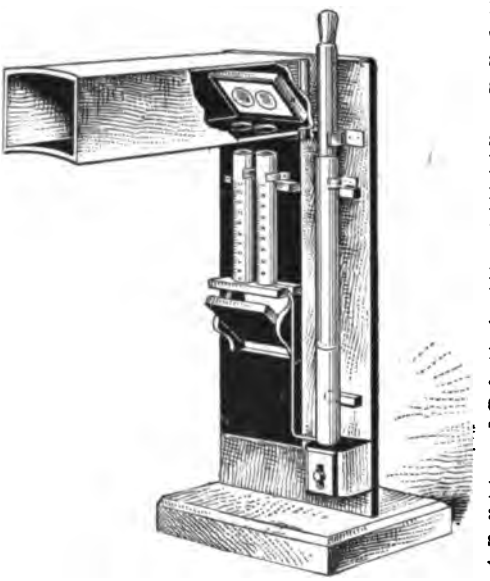


FIG. 69.—Colorimeter.

0.5 gram of TiO_2 is fused with about twenty times its weight of $KHSO_4$ in a platinum dish, keeping at fusion heat until the oxide has dissolved. A high temperature is not advisable. The fusion is dissolved in 5% sulphuric acid by gently heating. The solution washed into a 500-cc. graduated flask is made up to volume with 5% H_2SO_4. One cc. contains 0.001 gram TiO_2, or 0.0006 gram Ti.

Hydrogen Peroxide. Thirty per cent solution. If this is not available sodium peroxide dissolved in dilute sulphuric acid will do.

Apparatus. Colorimeter—Fig. 69. Also see Fig. 43, page 245.

Preparation of the Sample. The solution of the sample having been obtained by one of the procedures given under Preparation and Solution of the Sample, the element may be determined according to the procedure given below. If interfering substances are present, e.g., comparatively large amounts of iron, or if tungsten, vanadium or chromium are present it will be necessary to precipitate titanic acid by adding ammonium hydroxide to the boiling solution as directed under the gravimetric determination of the element. The washed precipitate is dissolved in sulphuric acid.

Procedure. The sulphuric acid solution of titanium should contain 5% of free sulphuric acid. It is poured from the beaker in which solution was effected into a 100-cc. Nessler tube, 2 cc. of hydrogen peroxide, 30% solution are added and the volume made up to 100 cc. with 5% sulphuric acid. The *standard* is prepared by pouring 40 or 50 cc. of 5% sulphuric acid into a second 100-cc. Nessler tube, adding 2 cc. of 30% hydrogen peroxide, H_2O_2, followed by sufficient

[1] Hillebrand.
[2] Dunnington, C. N., **64**, 302; J. A C. S., **12**, 210, 1891.

standard titanium solution to exactly match the sample and the solution made up to 100 cc. with 5% sulphuric acid. The titanium solution is added from a burette, noting the exact volume required. From this the percentage of titanium in the sample can readily be calculated. If iron is present in the sample, an equivalent amount should be added to the standard. If a colorimeter is used, a standard should be prepared which is deeper in color than the sample examined. The standard is poured into the comparison cylinder and the two tubes compared. By raising or lowering the plunger (see illustration) the standard solution is forced in or drawn out of the comparison tube. When the colors match, the cc. in the comparison tube will indicate the amount of TiO_2 present in the sample. The solution may be mixed by stirring with a platinum spiral.

Example. One-gram sample required 20 cc. of titanium standard solution, 1 cc. of which contained 0.001 gram TiO_2. Then the sample contains

$$\frac{0.001 \times 20 \times 100}{1} = 2\% \text{ } TiO_2.$$

If the colorimeter has been used and 150 cc. of standard made by adding 30 cc. of standard titanium solution and it is found that the column of liquor in the standard comparison tube stands at 85 cc., the calculation would be as follows: 150 cc. contains 30×0.001 gram TiO_2, therefore 85 cc. are equivalent to $\frac{85 \times 0.03}{150} = 0.017$ gram TiO_2 per gram or 1.7%.

For the practical application of the colorimetric method in determining titanium in steel the following procedure is given.

NOTE. *Separation of Titanium from Iron.* J. H. Walton, Jr.[1] separates titanium from iron by fusing the finely powdered substance with three or four times as much sodium peroxide, and extracts the fusion with water. The filtrate contains the sodium pertitanate whereas the iron oxide remains on the filter paper. The filtrate is acidified with H_2SO_4 until 5% of free acid is obtained and the color of this solution compared with a standard obtained by fusing a known weight of TiO_2 with Na_2O_2 and extracting and treating with H_2SO_4 as in case of the sample.

Colorimetric Determination of Titanium in Steel Treated with Ferro-carbon Titanium[2]

The titanium in steel treated with ferro-carbon titanium exists in two conditions:

(1) Titanium *insoluble* in hydrochloric acid.
(2) Titanium *soluble* in hydrochloric acid.

Of the very small amount of titanium in treated steel the greater part will usually be found in the first form, and ordinarily the determination of titanium in this form answers every purpose of identifying and judging the quality of titanium-treated steel.

When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble and it then is sometimes desirable to determine also that existing in the second form.

[1] J. Am. Chem. Soc., **29**, 481, 1907.
[2] By L. E. Barton. Method of analysis recommended by the Titanium A Manufacturing Company.

Reagents. ***Peroxide Solution.*** Dissolve 4 grams of sodium peroxide in 125 cc. dilute sulphuric acid (1 of acid to 3 of water), and dilute to 500 cc.

Concentrated Standard Titanium Solution. Stock Solution. One-fourth gram of a standard 20% carbonless ferro-titanium [1] is dissolved in 30 cc. dilute sulphuric acid (1 acid to 3 water). When solution is complete it is oxidized by the least possible quantity of concentrated nitric acid, boiled for a few minutes, cooled and diluted to such a volume that 1 cc. will contain 0.0005 gram of titanium.

When using a 5-gram sample 1 cc. is therefore equal to 0.01% titanium.

Dilute Standard Titanium Solution. This solution is made, just before making the determination, by diluting one volume of the concentrated standard titanium solution to ten volumes.

One cc. of this solution contains 0.00005 gram of titanium and is equal to 0.001% of titanium when using a 5-gram sample.

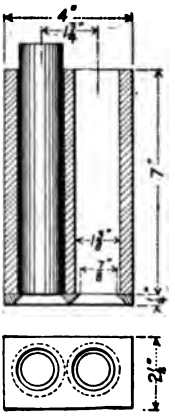


FIG. 70.

Apparatus. ***Pipettes and Burettes.*** The pipettes for measuring the concentrated standard solution and burette for delivering the dilute standard solution should be carefully calibrated.

Nessler Jars. These should be graduated with 50-cc. mark. It is convenient to have a set of four.

Colorimeter. The colorimeter or comparator consists of a rectangular block 2½ by 4 by 7 ins. high—the height being about ¾ in. less than the height of Nessler jars—through which two chambers 1⅝ ins. diameter and 1¼ ins. between centers are bored lengthwise—the chambers being of such diameter as to just receive the jars.

To one end of the block is fastened the base, which is ¼ in. thick and through which two ⅞-in. holes are bored concentric with the chambers, thus forming a shoulder which supports the jars and also exclude light from the sides of the tubes. To prevent shadows and give better lighting the holes in the base are beveled outward at an angle of 45°. The construction will be apparent by reference to Fig. 70. The interior of the chamber is painted dead black.

(a) For Determination of Titanium Insoluble in Hydrochloric Acid

Procedure. Dissolve 5 grams of steel in 100 cc. of dilute hydrochloric acid (one of concentrated acid to two of water) by boiling gently. Wash off the cover and wash down the sides of the beaker with water and filter out the slight insoluble residue, washing with hot water and dilute hydrochloric acid until free from iron. For filtration it is advisable to use either a close-grained paper or double rapid-filtering papers such as S. & S. No. 589 white ribbon.

Ignite the residue *gently* in a platinum crucible to burn off carbonaceous matter. Treat the residue in the crucible with a mixture of 3 cc. dilute sulphuric acid (1 : 1), 2 or 3 cc. hydrofluoric acid, and a few drops of nitric acid.

[1] Ferro-titanium suitable for the preparation of standard titanium solutions is made and supplied by the Titanium Alloy Manufacturing Company, Niagara Falls, N. Y.

Heat and evaporate to fumes of sulphuric anhydride to complete expulsion of hydrofluoric acid.

Cool, add a few cc. of water and heat until the solution is perfectly clear. The ignited residue may also be rapidly and completely brought into solution by fusion with about 3 grams of potassium bisulphate and dissolving the fusion in water and sulphuric acid.

In either case wash the contents of the crucible into one of a pair of Nessler jars and dilute with cold water nearly to the 50-cc. mark, and in the other jar place an equal volume of distilled water.

Place the jars in the colorimeter and observe if the sample solution is colorless. If the sample solution is colored slightly yellow by iron, the water in the standard tube should be brought to the same color by addition of a few drops of a ferric solution. For this purpose a solution of ferric ammonium sulphate, 30 grams per liter, is very convenient.

If the work up to this point has been carefully performed, the addition of ferric solution will usually be unnecessary; and if more than a few drops of ferric solution are required the analysis should be rejected and a new sample started. After adjusting the color—if necessary—bring the volume of solution in both jars to the 50-cc. mark.

The volumes now being equal and the solutions practically colorless, add 2 cc. of the peroxide solution to each. If the sample contains titanium even in minute quantity it will be indicated by the immediate development of a yellow color.

Match the colors by running into the standard jar freshly prepared *dilute standard* titanium solution, keeping the volumes equal by adding an equal quantity of water to the sample, placing the jars in the colorimeter for comparison of colors.

As before stated, each cc. of the dilute standard solution is equal to 0.001% titanium when using a 5-gram sample.

The determination may be made in less than an hour and requires little attention.

(b) For Determination of Titanium Soluble in Hydrochloric Acid

For the determination of soluble titanium the filtrate from the insoluble titanium residue obtained as before described may conveniently be used.

Dilute the solution in which the iron is already in the ferrous state to 180 cc. Add 10 cc. of alum solution made by dissolving 40 grams of crystallized alum in a liter of water.

The aluminum here added is subsequently precipitated as alumina with the titanium and serves to collect quickly the exceedingly small precipitate of titanium hydroxide and facilitate its separation from the solution by filtration.

Heat the solution to about 90° C. and add ammonia or ammonium carbonate solution, stirring constantly until a slight permanent precipitate is produced. Add dilute hydrochloric acid (1 to 1) drop by drop from the wash bottle until the precipitate is just redissolved and the solution perfectly clear; then add 1 cc. more of the dilute hydrochloric acid.

Add 3 cc. of phenylhydrazine dissolved in 10 cc. hot water, which will precipitate the titanium and aluminum. Stir thoroughly and filter immediately

on a 7-cm. filter paper in a Büchner funnel, using suction. Wash thoroughly with hot water.

Calcine the precipitate *gently* in a platinum crucible to destroy organic matter and dissolve the residue exactly as described under (*a*), except that 6 cc. of dilute sulphuric acid is used instead of 3 cc.

The solution, which has a very light yellow, or greenish-yellow color, is transferred to one of a pair of Nessler jars and diluted to the 50-cc. mark. About 40 cc. of water are placed in the other jar and the color of the sample solution exactly matched by addition of ferric ammonium sulphate and copper sulphate solutions, which are conveniently delivered from burettes.

For matching the original color of the solution nearly saturated solutions of ferric ammonium sulphate and copper sulphate are suitable.

Only a few drops of such solutions are required, but it is frequently necessary to use both blue and yellow to match the greenish-yellow tone of the sample solution.

The standard is finally diluted to the 50-cc. mark. The volumes now being equal and identical in color, add to each 2 cc. peroxide solution to develop the titanium color and finish the determination as before described under (*a*).

(c) For Determination of Total Titanium

The total titanium is given by the sum of the insoluble and soluble titanium determined as under (*a*) and (*b*); but if desired may be determined in one operation.

To determine total titanium, dissolve as before in hydrochloric acid and without filtering proceed as directed under (*b*) for determination of soluble titanium.

Determination of Titanium when Interfering Elements are Present

If chromium, vanadium or molybdenum is present in the steel, fuse the residue insoluble in hydrochloric acid or the calcined phenylhydrazine precipitate containing the interfering element with a mixture of sodium carbonate and a little sodium nitrate.

Dissolve the fusion in water and filter. The residue on the filter will contain the titanium, free from interfering element. Bring the residue into sulphuric acid solution by methods before described and determine the titanium as usual.

Colorimetric Determination of Titanium with Thymol[1]

Principal and Preliminary Considerations. Titanium dioxide dissolved in sulphuric acid is colored red by addition of thymol, the depth of color being directly proportional to the amount of titanium present. The intensity of the color is claimed by Lenher and Crawford to be twenty-five times that produced by hydrogen peroxide with the same amount of titanium.

As in case of hydrogen peroxide, fluorides destroy the color, hence must be absent. Dilution with water has no effect until the concentration of sulphuric acid falls below 79.4 (e.g., sp.gr. 1.725). The color then fades in direct propor-

[1] Victor Lenher and W. G. Crawford, C. N., **107**, 152, March 28th, 1913.

ion to dilution. Warm solutions are lighter in color than cold solutions with the ame amount of titanium, hence the standard and the sample compared must ave the same temperature. The color fades on heating but returns on cooling. The temperature should be kept below 100° C. Chlorides, phosphates and tin eem to have no effect. Tungsten, WoO_3, interferes, as it intensifies the color f the solution in direct proportion to the amount present; hence it must be emoved or allowance made by adding an equivalent amount to the standard r subtracting the equivalent blank.

Special Reagents. ***Thymol Solution 1%.*** The thymol is dissolved in a ittle glacial acetic acid containing 10% ethyl alcohol, and this solution added o concentrated sulphuric acid. Addition of the thymol directly to the acid would produce a colored solution. The reagent should be kept protected from strong light, otherwise it will become colored.

Apparatus. See Colorimetric Determination of Titanium with Hydrogen Peroxide, Figs. 69, 70, also Fig. 43.

Procedure. About 0.3 gram of the material is fused with potassium acid sulphate, $KHSO_4$, and the melt dissolved in concentrated sulphuric acid. Enough thymol reagent is added so that there is present at least 0.006 gram thymol for every 0.0001 gram TiO_2. Concentrated sulphuric acid is added to bring up the volume to 50 or 100 cc. in a Nessler tube exactly as in the case of the colorimetric determination of titanium with H_2O_2. The depth of color is compared with a standard solution of titanium dissolved in a concentrated sulphuric acid added to 5 cc. of thymol solution made up to a convenient volume with concentrated sulphuric acid. The procedure is the same as described in the H_2O_2 method.

THE ANALYSIS OF TITANIFEROUS ORES [1]

Determination of Titanium

Decompose the ore by fusion with potassium bisulphate, dissolving the fusion in water, hydrochloric and sulphuric acids. If an insoluble residue remains, filter it out. Calcine the residue, add a few drops of sulphuric acid and sufficient hydrofluoric acid to dissolve silica, evaporate to fumes of sulphuric anhydride and then heat to redness.

If a residue now remains, bring it into solution directly in acids or fuse with a little potassium bisulphate, etc., finally adding the solution to the main solution obtained as before described.

If desired, the sample of ore can first be partially dissolved in hydrochloric and sulphuric acids, and the insoluble residue then fused with potassium bisulphate or treated with sulphuric and hydrofluoric acids.

Some ores may be completely decomposed by a mixture of nitric, hydrofluoric and sulphuric acids, evaporating to fumes of sulphuric anhydride in a platinum dish to free the solution from nitric and hydrofluoric acids.

The complete decomposition of the sample having been accomplished, the titanium in the solution is determined by either the gravimetric or volumetric methods for Determination of Titanium in Ferro-Carbon Titanium. Pages 436 and 441.

[1] Method of Analysis used in the laboratories of The Titanium Alloy Manufacturing Company.

Determination of Iron in Presence of Titanium

The sample is decomposed as directed under the Determination of Titanium. The sulphuric acid solution, which should have a volume of 150 to 200 cc., is saturated with hydrogen sulphide gas to reduce the iron, and filtered to separate any precipitated sulphides and free sulphur. The filtrate is collected in a flask fitted with a rubber stopper through which pass two glass tubes, one reaching nearly to the bottom for conducting gas into the solution, the other a short exit tube. Unless the solution after filtration is still highly charged with hydrogen sulphide, more gas should be passed into the solution to reduce any iron that may have been oxidized by the atmosphere during filtration. The excess hydrogen sulphide is now expelled by boiling the solution while passing a current of carbon dioxide.

When the exit gases cease to darken a piece of filter paper moistened with lead acetate solution, the flask is cooled while still passing the carbon dioxide. When the flask has partially cooled the carbon dioxide is shut off and the flask quickly cooled in running water and immediately titrated with standard permanganate solution.

Determination of Silica

This determination is conveniently combined with the determination of iron, the ore being preferably decomposed by fusion with potassium bisulphate. The fusion is dissolved and evaporated with excess sulphuric acid to fumes of sulphuric anhydride and the silica determination finished as usual—weighing, volatilizing with hydrofluoric acid, etc. If the ore contains quartz or a silicate undecomposable by treatment with potassium bisulphate and hydrofluoric acid, the residue filtered from the sulphuric acid solution should be fused with sodium carbonate and the silica then determined as usual.

Determination of Alumina

After making determination or separation of titanium by *gravimetric* method use the filtrate for determination of alumina.

Phenylhydrazine Method for Determination of Aluminum in Presence of Iron

The iron and aluminum should be in hydrochloric or sulphuric acid solution. Nearly neutralize the solution with ammonium carbonate. Pass sulphurous acid gas to complete reduction of the iron. Boil until the excess sulphurous acid is driven off and if titanic acid separates filter it out.

After filtering out titanic acid again nearly neutralize with ammonium carbonate, pass a little sulphurous acid gas and heat for a few minutes to reduce any iron that might have been oxidized during filtration. If titanium has not been detected the second treatment with sulphurous acid may be omitted. In either case the solution still containing a little free sulphurous acid is nearly neutralized with ammonium carbonate, diluted to 300 cc. and 3 cc. of phenylhydrazine added. Stir thoroughly, let settle and filter out the alumina. If the precipitate is discolored by iron, dissolve in hydrochloric acid, and repeat the reduction, neutralization and precipitation by phenylhydrazine. Ignite and

weigh $Al_2O_3+P_2O_5$. Since the alumina precipitate may be contaminated by phosphoric anhydride (P_2O_5), determine it by analysis and correct the alumina determination accordingly.

Determination of Phosphorus

Phosphoric acid may be separated from titanic acid by repeatedly fusing the ore with alkali carbonate and extraction of alkali phosphate with water.

The determinations of other constituents of the ore are conducted by the usual methods of ore analysis.

TUNGSTEN, TANTALUM AND COLUMBIUM[1]

TUNGSTEN

WILFRED W. SCOTT

W., *at.wt.* 184.0; *sp.gr.* 18.77; *m.p.* 3000° C.;[2] *oxides*, WO_2 (*brown*); WO_3 (*yellow*); *acids*, H_2WO_4, *ortho tungstic*; $H_2W_4O_{13}$, *meta tungstic*

DETECTION

Minerals. The finely powdered material is fused with about six times its weight of potassium hydroxide in a silver or nickel crucible. (Fusion with Na_2CO_3 or with $KHSO_4$ in platinum will also decompose the material. See Solution of the Sample.) The cooled mass is extracted with hot water and filtered. The solution is treated with about 25 cc. of dilute hydrochloric acid and boiled. The precipitate formed may contain antimony, molybdenum, niobium, silica, tantalum, tin and tungsten. This is filtered and the moist residue treated with a solution of yellow ammonium sulphide. Antimony, molybdenum, tin and tungsten pass into the filtrate, niobium and tantalum remain on the filter. The ammoniacal sulphide extract is acidified with hydrochloric acid and boiled. The precipitate is filtered and washed with a little hydrochloric and nitric acids. Antimony, molybdenum and tin pass into the filtrate, while tungsten and sulphur remain on the filter. Tungsten is now confirmed as follows, portions of the precipitate being taken:

1. The residue is suspended in dilute hydrochloric acid and a piece of zinc, aluminum, or tin placed in the solution. In the presence of tungsten a blue-colored solution or precipitate is seen, the color disappearing upon dilution with water.

2. A portion of the precipitate is warmed with ammonium hydroxide and the extracts absorbed with strips of filter paper.

(*a*) A strip of this treated paper is moistened with dilute hydrochloric acid and warmed. In the presence of tungstic acid a yellow coloration is produced.

(*b*) A second strip of paper is moistened with a solution of stannous chloride. A blue color is produced in the presence of tungsten.

(*c*) A third strip dipped into cold ammonium sulphide remains unchanged until warmed, when the paper turns green or blue if tungsten is present.

Iron, Steel and Alloys. These decomposed with strong hydrochloric acid followed by nitric acid as directed under Solution of the Sample leave a yellow residue in the presence of tungsten. If this residue is digested with warm ammonium hydroxide and the extract evaporated to dryness a yellow compound, WO_3, will remain if tungsten is present. This oxide may be reduced in the reducing flame to the blue-colored oxide.

[1] Columbium is also known as Niobium.
[2] Circular 35 (2d Ed.), U. S. Bureau of Standards.

ESTIMATION

Tungsten occurs principally as wolfram, a tungstate of iron and manganese ($FeWO_4 \cdot MnO_4$), and as scheelite, a tungstate of calcium ($CaWO_4$). The best concentrate of hand-picked material contains 70 to 74% tungsten in terms of its oxide, WO_3.

The element is met with in alloys—ferro-tungsten,[1] silico-tungsten, tungsten steels containing as much as 10 to 20% of the metal, used for making high-speed, self-hardening cutting tools; tungsten powder;[1] alkali tungstates for mordanting purposes; tungstic oxide, WO_3; tungsten electric light filaments, etc.

Solution of the Sample

For solution of the sample the following facts should be kept in mind regarding solubilities.

The metal is practically insoluble in HCl and in H_2SO_4. It is slowly attacked by HNO_3, aqua regia and by alkalies. It is readily soluble in a mixture of HNO_3 and HF (=WF_6 or WOF_4).

Oxides. WO_2 is soluble in hot HCl and in hot H_2SO_4 (=red sol.), also in KOH (red sol.). The oxide WO_3 is scarcely soluble in acids, but is readily soluble in KOH, K_2CO_3, NH_4OH, $(NH_4)_2CO_3$, $(NH_4)_2S_x$. Both the acid and the alkali solutions deposit the blue oxide on standing.

Acids. Ortho tungstates. A few are soluble in water and in acids. The alkali salts only slightly soluble. The meta tungstates are easily soluble in water. Tungstates are precipitated from alkali salts by dilute H_2SO_4, HCl, HNO_3, H_3PO_4 (aqua) as yellow $WO_3 \cdot H_2O$ or white $WO_3 \cdot 2H_2O$. Meta tungstates are not precipitated by cold acids, but are precipitated by boiling and by long standing.

Solution of Minerals. Fusion Method. The material may be opened out by fusion with alkalies or alkaline carbonates, or by solution in mixtures of acids of which hydrofluoric acid is a constituent. The following procedure is satisfactory:

The finely divided mineral is fused with five or ten times its weight of sodium or potassium carbonate and the fusion extracted with hot water. The aqueous solution may contain one or more of the following: alkaline tungstate, niobate, molybdate, tantalate, arsenate, antimonate, stannate, aluminate, chromate, vanadate, silicate, phosphate, sulphate, chloride, fluoride, etc., in absence of combinations forming insoluble precipitates. The residue may contain alkaline zirconate, ferric oxide, carbonates of calcium, strontium, barium, etc. Tungsten

[1] TYPICAL ANALYSES

	Tungsten Powder	Ferro Tungsten
	%	%
W,	97 to 98.7	71 to 85.5
Fe,	.5 to .6+	14 to 24.5
C,	.1 to .3+	.4 to 2.6
Si,	.3 to .7+	.1 to .4
Mn,	0 to .2	.08 to .9+
P,	— —	.008 to .02
S,	— —	.01 to .02
Al,	.2 to .5	.001 to .07
Cu,	— —	0 to .008
Mg,	0 to .3+	

[illegible] nitrate precipitation [illegible] determination of th [illegible] may be necessary.)

[illegible] decomposed with hydrochlor [illegible] being removed in solution an [illegible] with a small amount of iron. The residu [illegible] extracted with water, an [illegible] Jones and Hodson recommended th [illegible]

[illegible] with 5 to 10 cc. of concentrate [illegible] is easily attacke [illegible] concentrated nitric acid the ferrou [illegible] until th [illegible] so long that some ferrou [illegible] of nitric acid as required, fo [illegible] and adding a slight excess the sampl [illegible] a few minutes. The essential points of th [illegible] sufficient hydrochloric acid to keep the tungsti [illegible] and maintaining the strength [illegible] The greater the excess of acid over neces [illegible] the greater the quantity of material, and of time occupied in [illegible] N [illegible] than is necessary to com- [illegible] If the acid solution of the metal is boiled [illegible] separate out, and then diluted with at least [illegible] and allowed to cool all the oxide is precipitated except [illegible] The [illegible] is generally contaminated with silica, which [illegible] with hydrochloric acid; and it contains traces [illegible] which may be estimated by fusion of the residue with sodium car- [illegible] extracting the tungsten with hot water; the iron remaining may be [illegible] and weighed and the weight subtracted from that of the previously weighed oxides WO_3 and Fe_2O_3.

In tungsten molybdenum steels 90 cc. of strong hydrochloric acid and 10 cc. of concentrated nitric acid are recommended. The solution is evaporated to pastiness, and then taken up and boiled with dilute hydrochloric acid (1 : 4), tungsten and silica remaining undissolved and molybdenum and iron passing into the filtrate.

Steel containing a high percentage of tungsten is extremely hard, so that it is practically impossible to get filings or borings without contaminating the sample with material from the cutting tool. The substance is best prepared by hammering into a coarse powder in a steel mortar. These coarse particles are not readily decomposed by the usual acid treatment or by the alkali carbonate and nitrate fusion. Opening up of the material may be easily accomplished by fusion with potassium acid sulphate.

About 0.5 gram of the coarse powder is heated with ten times its weight of $KHSO_4$ over a low flame, with covered crucible, the flame being removed if the action becomes violent. The melt is cooled slightly and an additional 5 grams of bisulphate added and the treatment repeated. Finally a third 5-gram portion of the acid sulphate is added and the material heated to a cherry redness for a

[1] "The Analysis of Steel-Works Materials."

few minutes. About fifteen or twenty minutes are sufficient to decompose the material. The heating should be conducted cautiously so that only a gentle evolution of gas occurs, and the mass kept in a molten state until the black particles of steel have entirely dissolved. The mass is now cooled, the crucible and cover placed in 50 to 75 cc. of water and boiled to disintegrate the fused mass. The liquid is treated with 20 cc. of concentrated hydrochloric acid until the precipitated tungstic acid is yellow. After settling, the precipitate is filtered off and washed with 10% ammonium nitrate solution. The residue is then dissolved in hot dilute ammonium hydroxide, the ammonium tungstate then evaporated in a weighed platinum crucible to dryness, then covered with a watch-glass and the residue heated to decompose completely the ammonium salt. Tungstic oxide, WO_3, remains and is so weighed.

Should silica be present in the sample it will contaminate the oxide, WO_3. It is removed by volatilization with hydrofluoric acid. A small amount of tungsten passes into the filtrate from the acid treatment, which is recovered by repeated evaporation with hydrochloric acid as described under the gravimetric procedure on page 453.

Ferro Tungsten Alloys may be dissolved by covering 1 to 2 grams of the alloy placed in a platinum dish with hydrofluoric acid and adding nitric acid in small portions, the dish being kept covered during the intervals between the additions. When the energetic action subsides 10 to 15 cc. of strong sulphuric acid are added and the material digested until the decomposition is complete. The mixture is now evaporated to SO_3 fumes over a low flame. (Air blown over the solution assists evaporation.) The residue is collected on a filter and washed well, then ignited and weighed as WO_3.

Tungsten Bronzes. About 0.5 gram of finely powdered bronze is heated in a porcelain crucible with 2 grams of alkali-free ammonium sulphate and 2 cc. of concentrated sulphuric acid, using a very small flame and occasionally agitating the mixture. After a few minutes an additional gram of ammonium sulphate and 1 cc. of sulphuric acid are added and the heating continued. The cooled fusion is moistened with water, rinsed into a porcelain dish, 50 cc. of concentrated nitric acid added and the contents digested for about four hours, then diluted with water and the tungstic oxide, WO_3, filtered off. The small amount of tungsten passing into the filtrate is recovered by evaporating to dryness and extracting the residue with hot dilute ammonium hydroxide. WO_3 is precipitated with HCl and the alkalies determined in the filtrate.

SEPARATIONS

One or more of the following separations may be required in the isolation of tungsten. (See Separation of Tungsten under Detection.)

Separation of Tungsten from Silica. The oxide of tungsten, as ordinarily obtained, is frequently contaminated with silica. The removal of silica is accomplished by heating the mixture in a platinum dish with sulphuric and hydrofluoric acids and volatilizing the silica. After taking to dryness and igniting gently, the last traces of sulphuric acid are expelled by adding ammonium carbonate and again igniting.

Separation from Tin. The method depends upon the fact that volatile stannic chloride is formed and expelled when stannic oxide is heated with ammonium

chloride, while the oxide of tungsten remains behind. The method was proposed by Rammelsberg.[1]

Silica having been removed, the weighed residue is mixed with six to eight times its weight of ammonium chloride (free from non-volatile residue) in a platinum crucible, placed in a larger crucible, both vessels being covered. Heat is applied until no more vapors of ammonium chloride are evolved. Additional ammonium chloride is added and the treatment is repeated three times. The fourth treatment is followed by weighing of the residue and the treatment repeated once more. If no further loss of weight takes place it is assumed that all the stannic oxide has been driven off. The inner crucible is now placed directly over the flame and heated to dull redness for a few minutes and the oxide, WO_3, weighed.

Separation of Tungsten from Tin and Antimony. Talbot's Process.[2] The mixed oxides are fused with twelve times their weight of potassium cyanide in a porcelain crucible. Tin and antimony are thrown out as metals and the soluble alkali tungstate formed. This is leached out with water and the aqueous extract boiled (hood) with an excess of nitric acid to drive off the cyanogen compounds. The tungstate is then precipitated by the usual methods. If phosphorus is present in the sample it will be found in the solution with tungsten and its removal will be necessary.

Separation of Tungsten from Arsenic and Phosphorus. Both arsenic and phosphorus may be precipitated by cold magnesia mixture in an ammoniacal solution, tungsten remaining in solution. The separation of arsenic is difficult, as it is tenaciously retained by tungsten as a complex salt. The following process is outlined by Kehrmann.[3]

One to 2 grams of the sample are fused with twice as much sodium hydroxide as is required to combine with the arsenic oxide, the resulting cake is dissolved in a little water and boiled in an Erlenmeyer flask for half an hour. After cooling, three times as much ammonium chloride as is needed to form chlorides with the alkalies present is added, and then ammonium hydroxide equal to one-fourth the volume of the solution under investigation, followed by sufficient magnesia mixture, added cold, drop by drop with constant stirring. After settling several hours, the solution is filtered and the residue washed with a weak solution of ammonia and ammonium nitrate. It is advisable to dissolve the residue in dilute acid and repeat the precipitation several times. The filtrates containing the tungsten are combined and concentrated by evaporation if necessary. The alkaline solution is neutralized with nitric acid and the tungsten precipitated with mercurous nitrate as described under the gravimetric procedures for tungsten, page 454. Magnesia is apt to contaminate the tungsten.

Separation of Tungsten from Molybdenum, Hommel's Process. The moist oxides[4] of tungsten and molybdenum are digested with concentrated sulphuric acid and a few drops of dilute nitric acid, in a porcelain dish over a free flame for about half an hour. About three times its volume of water is added to the cooled solution, the residue, WO_3, filtered off and washed with dilute sulphuric acid (1 : 20) followed by three washings with alcohol. The residue is ingited separately from the paper and weighed with the ash of paper as WO_3.

[1] Pogg. Ann., **120**, 66, 1864; C.N., **9**, 25, 1864.
[2] J. A. Talbot, J. Sci. (2), **50**, 244, 1870.
[3] F. Kehrmann, Ber., **20**, 1813, 1887.
[4] Ignited oxides require fusion with sodium carbonate, the resulting melt is then treated with sulphuric acid.

Molybdenum is in the filtrate and may be precipitated in a pressure flask with H_2S.

Volatilization of Molybdenum with Dry Hydrochloric Acid Gas. Péchard's Process.[1] The procedure depends upon the fact that molybdenum oxide heated in a current of dry hydrochloric acid gas at 250 to 270° C. is sublimed, whereas tungsten is not affected.

The oxides of the two elements, or their sodium salts, are placed in a porcelain boat and heated in a hard glass tube, one end of which is bent vertically downward and connected with a Péligot tube containing a little water. A current of dry hydrochloric acid gas is conducted over the material, heated to 250 to 270° C. From time to time the sublimate of molybdenum ($MoO_3 \cdot 2HCl$) is driven towards the Péligot tube by careful heating with a free flame. This enables the analyst to observe whether any more sublimate is driven out of the sample and to ascertain when the tungsten is freed of molybdenum. From one and a half to two hours are generally sufficient to accomplish the separation. If sodium salt is present it is leached out of the residue, and this is then ignited to WO_3. Molybdenum may be determined in the sublimate.

Separation from Vanadium.[2] Tungstic and vanadic acids are precipitated with $HgNO_3$ and HgO, the moist precipitate dissolved in HCl and the solution largely diluted; WO_3 is precipitated free from vanadium.

Separation from Titanium.[3] The material is heated with K_2CO_3 and KNO_3, tungsten is dissolved out with water and precipitated as mercurous tungstate.

Separation of Tungsten from Iron. The procedure is given under Solution of the Sample, of Steel and Alloys. The impure oxide WO_3 is fused with Na_2CO_3 and the melt extracted with water. $Fe(OH)_3$ remains on the filter. The filtrate is evaporated to dryness with HNO_3 and the residue extracted with water. The insoluble WO_3 is washed with dilute NH_4NO_3 solution, then dissolved in NH_4OH and tungsten determined in the solution.

GRAVIMETRIC PROCEDURES FOR DETERMINING TUNGSTEN

Since there is no highly commendable volumetric procedure for determining tungsten, the gravimetric methods are preferred.

The element is determined as tungstic oxide, WO_3. It may be isolated in the form of tungstic acid, ammonium tungstate, or as mercurous tungstate, in the usual course of analysis, all of which forms may be readily changed by ignition to the non-volatile oxide, WO_3.

Precipitation of Tungstic Acid

Isolation of tungstic acid by acid treatment of steels and alloys is given under Solution of the Sample in the procedures for these substances. If a fusion method with an alkali hydroxide or carbonate has been used for decomposition of the sample and the tungsten extracted with water the oxide may be precipitated as follows:

An equal volume of concentrated hydrochloric acid is added to the aque-

[1] E. Pechard, Comp. Rend., **114**, 173, 1891.
[2] Friedheim, C. N., **61**, 220.
[3] Defacqz, C.N., **74**, 293.

ous solution of the alkali tungstate, and the mixture evaporated to dryness on the water bath, and then heated for an hour or more in the hot-air oven at 120° C. The residue is moistened with hydrochloric acid, then taken up and boiled with water, filtered and washed with a 5% hydrochloric acid or ammonium nitrate solution. The precipitate is ignited and weighed as WO_3, which contains 0.793 gram of tungsten per gram of oxide.

NOTE. A small amount of tungsten may pass into the filtrate. This is recovered by repeated evaporation with hydrochloric or nitric acids.

Precipitation of Tungsten as Mercurous Tungstate. Berzelius' Process[1]

The water extract of the sodium carbonate fusion is concentrated to 50 to 100 cc., a few drops of methyl orange added and the alkali carefully neutralized with nitric acid, avoiding an excess.[2] The mixture is boiled to expel all the carbonic acid, then cooled and an excess of mercurous nitrate added. (Usually 20 cc. of a solution made by digesting 60 grams of mercury with 25 cc. of nitric acid (sp.gr. 1.4)+75 cc. of water two hours on steam bath, and diluting to 400 cc.) When the precipitate settles the supernatant solution should be clear. After two hours or more the yellow precipitate is filtered off, washed with 2% mercurous nitrate solution, dried and ignited to WO_3.

One gram WO_3 = 0.793 gram W.

Volumetric Method[3]

Tungstic oxide is precipitated according to one of the procedures outlined in the section on Solution of the Sample. The impure oxide containing silica and iron is washed on the filter with dilute nitric acid, then with dilute solution of potassium nitrate (5–10% sol.) until the filtrate shows the residue is freed from acid. The residue is washed into a flask, 200 cc. of water added and the mixture titrated boiling hot with standard solution of sodium hydroxide, using phenolphthalein as indicator.

One cc. N. NaOH = 0.116 gram WO_3, or = 0.092 gram W.

[1] J. J. Berzelius, Schweigger's Jour., **16**, 476, 1816; W. W. Hutchin, Analyst. **36**, 398, 1911.

[2] Mellor recommends adding a few drops of nitric acid in excess, followed by the mercurous nitrate, and then ammonium hydroxide, drop by drop, until a brown precipitate separates.

[3] Herting, Z. angew. Chem., **14**, 165, 1901.

TANTALUM AND COLUMBIUM

Cb, *at.wt.* 93.5; *sp.gr.* 7.06; *m.p.* 1950°; *oxides* CbO, CbO_2, Cb_2O_5.
Ta, *at.wt.* 181.5; *sp.gr.* 14.49; *m.p.* 2900°; *oxides* TaO_2, Ta_2O_4, Ta_2O_5.

DETECTION

The finely powdered mineral is digested with strong hydrochloric acid, followed by concentrated nitric acid and the mixture taken to dryness. The residue is treated with hydrochloric acid, diluted with water, boiled and filtered. The residue is digested with warm ammonium hydroxide to remove tungsten and the solution filtered from the insoluble material, in which tantalum and columbium will be found, if present in the sample.

Decomposition of the material may be effected according to the procedure described for the detection of tungsten, page 448.

The residue obtained is digested, in a platinum crucible, with hydrofluoric acid and a saturated solution of potassium fluoride added. The mixture is evaporated to small volume and allowed to cool slowly. Tantalum will separate in acicular rhombic crystals (solubility—1 part of the salt in 200 parts of water) as potassium fluotantalate $2KF \cdot TaF_5$; columbium separates in plates as the double fluoride, $2KF \cdot CbF_5$, if HF is in excess, or as a double oxy-fluoride $2KF \cdot CbOF_5$, if HF is not in excess; the columbium salt being much more soluble (1 part of the salt in 12 parts of water) crystallizes after the crystals of tantalum have formed.

The crystals may be examined under a lens and then treated as follows: The needle-like crystals are heated in a shallow platinum dish or crucible cover with strong sulphuric acid to fumes, the cooled mixture is transferred to a test-tube with water and boiled to precipitate the tantalic acid. An opalescent solution is obtained when this precipitate is treated with an excess of hydrochloric acid. Metallic zinc added to this solution produces no color. A light-brown precipitate is obtained with tannic acid in the presence of tantalum. If the crystals of columbium salt are treated in the same way, metallic zinc added to the acid solution will give a blue coloration, and tannic acid an orange-red coloration. Tantalic acid fused with sodium meta-phosphate gives a colorless bead (distinction from silica). The bead moistened with $FeSO_4$ and heated in the inner flame is not colored red. Columbic acid fused in the same way gives a blue bead in the reducing flame, and a red bead by addition of $FeSO_4$, and heating in the flame.

ESTIMATION

Tantalum and columbium occur commonly with tungsten in nature. In the following minerals, however, tantalum and columbium form the more important constituents:

Columbite, $(Ta \cdot Cb)_2(Fe \cdot Mn)O_6$; pyrochlore, $RCb_2O_6R(Ti \cdot Th)_2$; hatchettolite, $2R(Cb \cdot Ta)_2O_6$ or $R_2(Cb \cdot Ta)_2O_7$; fergusonite, $R(Cb \cdot Ta)O_4$; yttrotantalite, $RR(Cb \cdot Ta)_4O_{15} \cdot 4H_2O$; samarskite, $R_3R_2(Cb \cdot Ta)_6O_{21}$.

Tantalum is used in electric light filaments; it is also used for hardening steel for drills, files, cutting edges, watch springs, and pen points. It is used in rectifiers for alternating currents.

Solution of the Sample

The statements made for solution of the sample in determinations of tungsten apply here also. It is well to keep the following facts in mind: Tantalum is insoluble in the common mineral acids—hydrochloric, nitric and sulphuric acids, but dissolves in hydrofluoric acid. Columbium is insoluble in hydrochloric, nitric and in nitro-hydrochloric acid, but dissolves in hot concentrated sulphuric acid. The oxides Ta_2O_5 and Cb_2O_5 fused with KOH form soluble salts. Cb_2O_5 (not strongly ignited) is soluble in acids, from which $(NH_4)_2S$ and NH_4OH precipitate columbic acid (containing ammonia). Freshly precipitated tantalic acid is soluble in acids, and reprecipitated by NH_4OH. The acid dissolves readily in HF.

Tantaliferous Minerals. Although decomposition may be effected by fusion with potassium acid sulphate, fusion with potassium hydroxide is recommended as being the best flux for opening the minerals. Simpson's process is as follows:[1]

Three grams of pure potassium hydroxide are fused in a nickel or silver crucible and the finely powdered mineral (0.5 gram) added, the contents mixed by gently rotating the crucible and fusion kept at a dull red heat for ten minutes longer. The crucible placed in a hole in an asbestos board, Fig. 65, is heated over a free flame for half an hour, the sample being covered. The lid is removed and allowed to cool reversed, if any material clings to this. The cooled crucible, placed in a beaker, is two-thirds filled with distilled water, and a clock-glass immediately placed over the beaker. After the violent reaction has subsided the contents of the crucible are poured into about 10 cc. of dilute hydrochloric acid (sp.gr. 1.08) in a 300-cc. beaker, and the crucible, basin and the lid washed with water, followed by about 20 cc. of the dilute acid, and again with water, adding the washings to the remaining solution. The total volume of the solution should occupy from 80 to 100 cc. A drop or two of alcohol are added to destroy any potassium manganate formed.

Separations

Isolation of Columbium and Tantalum Oxides. Separation from iron, manganese, copper, cobalt, nickel, calcium, magnesium, titanium, and tin. The solution obtained above is boiled with 5 to 10 cc. of hydrochloric acid (sp.gr. 1.16) (less acid may be used if titanium is absent). Columbium and tantalum hydroxides are precipitated. The solution is now diluted to 200 cc. and boiled for fifteen minutes longer to make sure that the precipitation is complete. After settling, the clear solution is decanted through a close-grained filter and the residue, having been transferred to the filter, is washed with dilute hydrochloric acid (sp.gr. 1.08) until the washings give no indication of iron. The residue may contain tantalum, columbium, tungsten, silica, antimony and tin. The greater part of the tin, titanium, and all of the iron, manganese, cobalt, nickel, copper, calcium and magnesium are removed in the filtrate.

NOTES. If the filtrate becomes turbid, it is advisable to dilute the solution and repeat the boiling to recover the columbium and tantalum that may still be in solution.

In the presence of appreciable amounts of titanium a soluble double chloride of columbium and titanium is formed, so that the precipitation of columbium

[1] E. S. Simpson, Chem. News, **99**, 243, 1909.

is not complete. (See L. Weiss and Landecker, Chem. News, 101, 2, 13, 26, 1910.) The formation of this compound is hindered by the addition of an oxidizing agent—sodium nitrate—to the alkali.

Removal of Tin, Antimony, Tungsten and Silica. ***Tungsten*** is removed by digesting the moist precipitate with ammonium hydroxide or sulphide, tungsten being soluble in these reagents. Antimony and Tin are also removed.

Silica is volatilized by heating the residue with sulphuric and hydrofluoric acids according to the standard procedure.

Tin. The oxide may be reduced with hydrogen passed over the heated residue within a boat placed in a combustion tube. The tin may now be dissolved out with hydrochloric acid.

Determination of Columbium and Tantalum

The insoluble residue obtained, freed from other elmeents by the procedures outlined, is ignited at a red heat for fifteen or twenty minutes and the residue weighed as $Cb_2O_5+Ta_2O_5$.

URANIUM

WILFRED W. SCOTT

U, *at.wt.* 238.5; *sp.gr.* 18.7; *m.p.* <1850° C.;[1] *oxides* UO_2, UO_3, (*oxide* U_3O_8, *formed by ignition* $= UO_2 + 2UO_3$)

DETECTION

The mineral is warmed with a slight excess of nitric acid (1 : 1) until decomposition is complete. The solution is diluted with water and then an excess of sodium carbonate added and the mixture boiled and filtered. Sufficient nitric acid is added to neutralize the carbonate, and after expelling the CO_2 by boiling, sodium hydroxide is added to the filtrate. A yellow precipitate is formed in presence of uranium. The precipitate is insoluble in an excess of the reagent, but dissolves in the ammonium carbonate.

Uranous salts are green or blue and form green or bluish-green solutions, from which alkalies precipitate uranous hydroxide, reddish brown, insoluble in excess, but readily dissolved by ammonium carbonate. Uranous salts are strong reducing agents.

Uranyl salts ($UO_2 \cdot R_2$) are yellow. Alkali carbonates give a yellow precipitate, soluble in excess. UO_2 is regarded as a basic radical, known as "uranyl." The radical migrates to the cathode, upon electrolysis of a uranyl solution. Uranyl salts are more stable than uranous and are better known.

ESTIMATION

The element occurs in the following minerals:[2]

Pitchblende, or uraninite, containing 40 to 90% U_3O_8.
Autunite, $Ca(UO_2)_2P_2O_8 \cdot 8H_2O$, contains 55 to 62% UO_3.
Torbernite, $Cu(UO_2)_2 \cdot P_2O_5 \cdot 8H_2O$, contains 57 to 62% UO_3.
Carnotite, a vanadate of potassium and uranium, $V_2O_5 \cdot U_2O_3 \cdot K_2O \cdot 3H_2O$.
Samarskite, a urano-tantalate of iron and yttrium, etc., 10 to 13% UO_3.
Fergusonite, a columbate of cerium, uranium, yttrium, calcium and iron.

Nearly all the silicates, phosphates and zirconates of the rare earths contain uranium.

The element is used in the ceramic industry for producing yellow, brown, gray, and velvety-black tints. It produces canary-yellow glass. It is used as a mordant in dyeing of silk and wool. It also finds use in photography. The metal is used in cigarette-lighters and self-lighting burners.

[1] Circular 35 (2d Ed.), U. S. Bureau of Standards.
[2] Thorp, "Dictionary of Applied Chemistry," Longmans, Green & Co. Cahen and Wootten, "The Mineralogy of the Rarer Metals," Chas. Griffin & Co. and J. B. Lippincott Co.

Preparation and Solution of the Sample

The element dissolves in hydrochloric and in sulphuric acids; less readily in nitric acid. It is insoluble in alkaline solutions.

The oxide, UO_2, dissolves in nitric acid and in concentrated sulphuric acid.

The salts, UF_4 and $UO_2(HPO_4)_2 \cdot 4H_2O$, are insoluble in water, but dissolve in strong mineral acids.

Solution of Ores. One gram or more of the ore is dissolved with 15 to 20 cc. of aqua regia, by placing the mixture first on the steam bath for ten to fifteen minutes and then gently boiling over a low flame or on the hot plate. The solution is taken to dryness, silica dehydrated as usual, the residue treated with 10 cc. of hot dilute hydrochloric acid and diluted to about 50 cc. with hot water and the silica filtered off. Uranium passes into the filtrate. The solution is now treated as directed under Separations. If much silica or acid-insoluble matter is present, this should be treated in a platinum dish with strong hydrofluoric acid, and evaporated twice on the steam bath with hydrochloric acid to expel HF. The residue, dissolved with hydrochloric acid and water, is added to the first portion of solution obtained.

SEPARATIONS

Separation of Uranium from Copper, Lead, Bismuth, Arsenic, Antimony and the Other Members of the Hydrogen Sulphide Group. The solution containing uranium, etc., having an acidity of about 5 cc. strong HCl per 100 cc. of solution, is saturated with hydrogen sulphide and allowed to settle and again saturated with H_2S. The sulphides are filtered off and washed. The filtrate and washings contain the uranium that was present in the sample.

Separation of Uranium from Iron and from Elements Having Water-insoluble Carbonates. The filtrate from the hydrogen sulphide group is concentrated to about 150 cc., and 15 cc. of hydrogen peroxide added. The solution is now neutralized with sodium carbonate and about 3 grams added in excess. After boiling for about twenty minutes, renewing the water evaporated, the hydroxide of iron, insoluble carbonates, etc., are filtered off, washed with hot water and the filtrate set aside for the determination of uranium. To recover any occluded uranium the precipitate is dissolved in just sufficient nitric acid to effect solution, and iron again precipitated by addition of hydrogen peroxide and sodium carbonate and boiling as directed above. The combined filtrates from this precipitate are concentrated to about 250 cc.

Separation of Uranium from Vanadium. Procedure 1. ***To be Used in the Determination of Uranium.*** The solution obtained as directed, under the previous separation, is acidified with nitric acid, adding a slight excess, and CO_2 expelled by boiling. The acid is now neutralized with ammonia (a slight permanent precipitate appearing), and then 10 cc. of strong nitric acid is added (total volume about 280–300 cc.). Vanadium is now precipitated as lead vanadate by adding 10 cc. of a 25% solution of lead acetate, followed by sufficient strong ammonium acetate solution (1 vol. strong NH_4OH+1 vol. H_2O+sufficient glacial acetic acid to neutralize NH_4OH) to neutralize the free nitric acid. The precipitated vanadate, which is insoluble in the acetic acid formed by the reaction, is allowed to settle for a couple of hours on the steam bath and is then filtered off and washed once, the uranium passing into the filtrate. To recover any occluded uranium

the precipitate is dissolved in the least amount of nitric acid required, the solution neutralized with ammonia, diluted to about 100 cc. and 5 cc. nitric acid added followed by 2 to 3 cc. of lead acetate solution. The vanadate of lead is again precipitated by neutralizing the free acid with ammonium acetate. The vanadate is filtered off and washed with warm water. The filtrate containing the uranium is concentrated to about 400 cc.

In order to remove the lead present in the filtrate, due to the excess of the acetate reagent, about 10 cc. of strong sulphuric acid are added, the bulk of the lead precipitated as the sulphate is filtered off, and the $PbSO_4$ washed with cold water. The filtrate is neutralized with ammonia and freshly prepared $(NH_4)HS$ added until the solution appears yellow and the remaining lead and all the uranium are thrown out as sulphides. The precipitate is allowed to settle on the steam bath, and then filtered off and washed with a small amount of warm water. This is now dissolved with hot dilute nitric acid (1 : 2), and the nitric acid then expelled by taking the solution to SO_3 fumes with about 5 cc. of strong sulphuric acid. The cooled residue is taken up with cold water, boiled and the lead sulphate allowed to settle until the solution is cold. The precipitate is filtered off and washed with water slightly acidified with sulphuric acid. Uranium passes into the filtrate. If alumina is present in the sample it must now be removed according to the directions following Procedure 2, before precipitation of uranium.

Procedure 2. ***To be Used in the Volumetric Determination of Uranium.*** The separation of vanadium from uranium may be effected by precipitation of the latter as a phosphate according to the following procedure. The solution is heated and allowed to run in a small stream through a funnel with constricted stem, into a boiling solution of 15 grams of ammonium acetate, 5 grams of microcosmic salt dissolved in 100 cc. of water containing about 5 cc. of glacial acetic acid. A rod, with a cup-shaped tip, placed in the solution prevents bumping. The mixture is allowed to boil for a few minutes, the beaker is then removed from the heat and the precipitate allowed to settle. This is now transferred to a filter after first decanting off the clear solution. It is washed once with hot water, then washed back into the beaker and dissolved in a small amount of hot dilute nitric acid, the precipitate clinging to the filter being dissolved off by the acid, which is allowed to run through the filter into the beaker. This nitric acid solution containing the vanadium is diluted to about 75 cc. and the uranium (together with aluminum if present) again precipitated as the phosphate according to the procedure described. The precipitate is again transferred to the filter previously used, and washed off with hot water four or five times. Vanadium passes into the filtrate. The phosphate is now dissolved off the filter with 15 cc. of hot dilute sulphuric acid (1 : 3), and uranium determined by titration with permanganate according to the directions given under the volumetric method described later.

Removal of Alumina in the Gravimetric Method for Determining Uranium. Alumina would interfere in the gravimetric method, hence its removal is necessary if present. The filtrate obtained after removal of iron and freed from vanadium, if this is present in the original sample, is nearly neutralized with ammonia. Now sufficient powdered ammonium carbonate is added to the cooled solution to precipitate the alumina and react with the uranium, and about 2 grams in excess. If the precipitate is bulky and is at all yellow, it is dissolved in a little sulphuric acid and again precipitated as before. The aluminum hydroxide is filtered off and washed with hot water. Uranium is determined in the filtrate.

GRAVIMETRIC DETERMINATION OF URANIUM AS THE OXIDE, U_3O_8

Procedure. The filtrate containing the uranium, as obtained according to the method given, is made slightly acid with hydrochloric or sulphuric acid and boiled to expel the CO_2. Ammonium hydroxide (free from carbonate) is now added in slight excess and the solution brought to boiling. The precipitate is allowed to settle, then filtered onto filter paper or into a weighed Gooch crucible and washed five or six times with a 2% solution of ammonium nitrate and finally once with water. It is now dried and ignited to the oxide U_3O_8, in which form it is weighed.

$$U_3O_8 \times 0.8482 = U.$$

NOTES. The purity of the oxide may be ascertained by dissolving in HNO_3 and testing for vanadium with H_2O_2 and for Al_2O_3 by adding $(NH_4)_2CO_3$.

Treadwell recommends that the oxide be reduced by hydrogen passed over the red-hot residue, the brown UO_2 being formed. The oxide is cooled in a current of hydrogen.

VOLUMETRIC DETERMINATION OF URANIUM BY REDUCTION AND OXIDATION

Introduction. The determination of uranium by oxidation of the lower oxide UO_2 to UO_3 may be accomplished with great accuracy by means of permanganate in precisely the same manner as in the determination of iron, the Jones reductor being used for the reduction of the uranic salt to the uranous form. The metal must be in solution either as a sulphate, a chloride or an acetate, but not as a nitrate. If present as a chloride the usual preventative solution of phosphoric acid and manganous sulphate solution must be present as in case of the titration of a chloride of iron, hence a sulphate solution is to be preferred. Although the degree of reduction varies with conditions, it is found that with brief contact with the oxygen of the air the oxide UO_2 is formed.

Procedure. Solution. The method for preparation of the sample, isolation of the uranium, has been given under Preparation and Solution of the Sample and Separations. The solution from the ammonium carbonate precipitate is acidified with sulphuric acid and boiled to expel the CO_2.

Reduction. The uranium sulphate solution, diluted to a volume of 100 to 150 cc., containing one-sixth of its volume of sulphuric acid, is heated nearly to boiling and the organic matter that may be present oxidized by addition of just sufficient potassium permanganate solution to produce a faint pink color. Fifteen to 20 cc. of dilute sulphuric acid are passed through the 18-in. column of zinc in the Jones reductor, followed by the hot uranium sulphate solution, flowing very slowly, fifteen to twenty-five minutes being required for 0.2 gram uranic oxide, thirty to forty minutes for 0.3 gram of the oxide, care being taken that the liquid in the reductor always covers the zinc.[2] The uranic solution is followed by 10 to 15 cc. of dilute 1 : 6 solution of sulphuric acid.

[1] Oxidation of lower oxides by air to UO_2". O. S. Pulman, Jr. Am. Jour. Sc. (4), 16, 229.

[2] Hydrogen dioxide formed by nascent hydrogen in contact with air would vitiate results.—Gooch.

Titration. The olive-green solution is poured into a beaker or casserole. The lower oxides are immediately oxidized to UO_2 by the air, as seen by the slight change of color to sea green. The hot solution is now titrated with tenth normal permanganate. The solution during titration gradually becomes more and more yellowish green, as the highest oxidation is approached, until a faint pink color is obtained. With large amounts of uranium the color appears a yellowish pink.

One cc. N/10 $KMnO_4$ = 0.11925 gram U.

NOTE. 55.85 grams Fe is equivalent to 119.25 grams U.—Sutton.

VANADIUM

WILFRED W. SCOTT

V, *at.wt.* 51.0; *sp.gr.* 6.025; *m.p.* 1720° C.;[1] *oxides* V_2O, V_2O_2,[2] V_2O_3, V_2O_4, V_2O_5; *vanadates—meta* $NaVO_3$, *ortho* Na_3VO_4, *pyro* $Na_4V_2O_7$, *tetra* $Na_2HV_6O_{17}$, *hexa* $Na_2H_3V_6O_{17}$.

DETECTION

Ammonium Sulphide or Hydrogen Sulphide passed into an ammoniacal solution of vanadium precipitates brown V_2S_5, soluble in an excess of alkali sulphide and in alkalies, forming the brownish-red thio- solution, from which the sulphide may be reprecipitated by acids.

Reducing Agents. Metallic zinc, sulphites (SO_2), oxalic acid, tartaric acid, sugar, alcohol, hydrogen sulphide, hydrochloric acid, hydrobromic and hydriodic acids (KI) reduce the acid solutions of vanadates with formation of a *blue-colored* liquid.[3] (See Volumetric Methods.) Reduction is hastened by heating.

Hydrogen Peroxide added to a cold acid solution of vanadium produces a *brown color*, changing to blue upon application of heat.

Solid Ammonium Chloride added to a neutral or slightly alkaline solution of a vanadate precipitates the colorless, crystalline salt, NH_4VO_3, insoluble in ammonium chloride. The ammonium metavanadate ignited is decomposed, ammonia volatilizing and the red pentoxide of vanadium remaining as a residue. *V_2O_5 is distinguished from Fe_2O_3* by the fact that it fuses very readily with the heat of Bunsen burner, whereas the oxide of iron, Fe_2O_3, is infusible in the heat of a blast lamp. M.p. $V_2O_5 = 658°$ C.; m.p. $Fe_2O_3 = 1548°$ C.

Comparison of Vanadium and Chromium Salts. Vanadium, like chromium, forms a soluble salt upon fusion with sodium carbonate and potassium nitrate, or with sodium peroxide. The solution of ortho, tetra and hexa vanadate and those of chromates are yellow or orange; the color of the chromate, however, becomes more intense when acidified, whereas that of the vanadate is reduced. The lead and barium salts precipitated from neutral or slightly acetic acid solution are similar in appearance. A greater contrast exists between the mercurous and silver salts. Silver nitrate, for example, produces a dark-maroon precipitate with a soluble chromate and an orange-colored precipitate with a vanadate; mercurous nitrate produces a red-colored precipitate with chromates and a yellow with vanadates. *Vanadates are best distinguished from chromates by the reduction test;* reducing agents such as a soluble sulphite, or sulphurous acid added to acid solutions, form *a blue-colored liquid with vanadates and a green color with chromates. Ammonium hydroxide* added in excess of the cold reduced solutions gives a brown

[1] Circular 35 (2d Ed.), U. S. Bureau of Standards.

[2] V_2O_2 forms vanadyl salts.

[3] Reduction with zinc is rapid with vanadates, much less vigorous with chromates. V_2O_5 reduced to V_2O_2, color changes to blue, green, lavender and finally violet. SO_2 or H_2S reduces V_2O_5 to V_2O_4.

color, or a brown to dirty green precipitate with *vanadium*, and violet or lavender color or a light green-colored precipitate with *chromium*, depending upon the concentration of the solutions. Hydrogen peroxide added to the reduced cold acid solutions changes the vanadium blue to reddish brown; the chromium green remains unchanged.

Detection of Vanadium in Steel. Five grams of the sample are dissolved in dilute nitric acid, the nitrous fumes boiled off, the solution cooled, and an excess of sodium bismuthate added. After filtering through an asbestos filter an excess of concentrated ferrous sulphate solution is added, and the solution divided into two equal parts in test-tubes. To one portion 10 cc. of hydrogen peroxide are added and to the other 10 cc. of water. If vanadium is present the peroxide solution will show a deeper color than the untreated solution. A deep red color is produced with high vanadium steels and a brownish-red with low. Since titanium also causes this color, it would interfere, if it were not for the fact that the color produced with titanium is destroyed by hydrofluoric acid and fluorides, whereas that of vanadium is not. In presence of titanium, 5 cc. of hydrofluoric acid are added to the treated sample.

The brown color produced by hydrogen peroxide, with vanadium solutions, will remain in the water portion when shaken with ether. The ether layer is colored a transient blue in presence of chromium.

ESTIMATION

The materials in which the estimation of vanadium is desired may be surmised from the following facts: Industrial application. Vanadium is used in special iron and steel alloys. It increases the strength of steel as well as the compression power, without loss of hardness, and increases the resistance to abrasion; hence vanadium steels are used in locomotive and automobile cylinders, pistons, bushings and in all parts of machines subject to jar. It is used in high-speed tools, vanadium bronzes for gears, trolley wheels, etc. It is used in indelible inks, and in the form of alkali vanadates and hypovanadates it serves as a mordant for aniline black on silk, for calico printing and like uses. Vanadium salts are used in ceramics where a golden glaze is desired.

The element occurs widely distributed in minute quantities. It is found in iron ores, hence occurs in blast-furnace slags as the oxide, V_2O_5. The principal ores are:

Patronite, a sulphide of vanadium containing 28 to 34% V_2O_5, associated with pyrites and carbonaceous matter; the principal source of vanadium.

Vanadinite, $(PbCl)Pb_4(VO_4)_3$, containing 8 to 21% V_2O_5.

Carnotite, $K_2O \cdot 2UO_2 \cdot V_2O_5 \cdot 3H_2O$, contains 19 to 20% V_2O_5.

Descloizite, $(PbZn)_2NVO_5$, contains 20 to 22% V_2O_5.

Roscoelite, a vanadium mica with variable composition.

Eusynchite, contains 17 to 24% V_2O_5.

Cuprodescloizite, $(PbZnCu)_2(OH)VO_4$, contains 17 to 22% V_2O_5.

Calciorolborthite, $(CuCa)_2(OH)VO_4$, contains 37 to 39% V_2O_5.

Vanadium occurs in ores of copper and lead, it is present in certain clays and basalts, in soda ash, phosphate soda, and in some hard coals.

Preparation and Solution of the Sample

In decompositon of the material for analysis the following facts regarding the solubility of the metal, its oxides and principal salts, will be helpful:

Element. The metal is not attacked by aqueous alkalies, but is soluble by fusion with potassium or sodium hydroxide, and sodium carbonate containing potassium nitrate. It is insoluble in dilute hydrochloric and sulphuric acids. It dissolves in concentrated sulphuric acid and in dilute and concentrated nitric acid forming blue solutions.

Oxides. V_2O_2 is easily soluble in dilute acids, giving a lavender-colored solution.

V_2O_3 is insoluble in hydrochloric and sulphuric acids, and in alkali solutions. It dissolves in hydrofluoric acid, and in nitric acid.

V_2O_4 is easily soluble in acids, forming blue-colored solutions. It dissolves in alkali solutions.

V_2O_5 is soluble in acids, alkali hydroxide and carbonate solutions. Insoluble in alcohol and acetic acid.

Salts. Ammonium meta vanadate, NH_4VO_3, is slightly soluble in cold water, readily soluble in hot water. The presence of ammonium chloride renders the salt less soluble. The vanadates of lead, mercury and silver are difficultly soluble in water. These are dissolved, or are transposed by mineral acids, the vanadium going into solution; i.e., lead vanadate treated with sulphuric acid precipitates lead sulphate and vanadic acid passes into solution.

General Procedure for Decomposition of Ores. One gram (or more) of the finely divided material is placed in a large platinum crucible together with five times its weight of a mixture of sodium carbonate and potassium nitrate ($Na_2CO_3 = 10$, $KNO_3 = 1$). The product is heated to fusion over a blast lamp and, when molten, about 0.5 to 1 gram more of the nitrate added in small portions. (Caution—platinum is attacked by KNO_3. A large excess of Na_2CO_3 tends to prevent this.) The material should be kept in quiet fusion for ten to fifteen minutes, when most of the ores will be completely decomposed. The cooled fusion is extracted with boiling water, whereby the vanadium goes into solution. Arsenic, antimony, phosphorus, molybdenum, tungsten and chromium pass into solution with the vanadium. These must be removed in the gravimetric determination of this element. (Iron remains insoluble in the water extract.)

Should there be any undecomposed ore, the residue from the water extract will be gritty. If this is the case, a second fusion with the above fusion mixture should be made.

Small amounts of occluded vanadium may be recovered from the water-insoluble residue by dissolving this in nitric acid and pouring the solution into a boiling solution of sodium hydroxide. Vanadium remains in solution.

Vanadium may be determined volumetrically after removal of the hydrogen sulphide group, by titration with potassium permanganate according to the procedure given later. The isolation and determination of vanadium by the gravimetric procedures are given in detail later.

Ores and Material High in Silica. The sample is treated in a platinum dish with about ten times its weight of hydrofluoric acid (10 to 50 cc.) and 2 to 5 cc. of strong sulphuric acid. The silica is expelled as SiF_4 and the hydrofluoric acid driven off by taking the solution to SO_3 fumes. The residue is extracted with hot water containing a little sulphuric acid. Any undissolved residue may be brought

into solution by fusion with potassium acid sulphate, $KHSO_4$, and extraction with hot water containing a little sulphuric acid. By this treatment the iron passes into solution with vanadium.

Products Low in Silica. Decomposition may be effected by fusion in a nickel crucible with sodium peroxide and extraction with water. The water should be added cautiously, as the reaction is vigorous. One gram of the finely divided ore is intimately mixed with 3 to 4 grams of Na_2O_2 and 1 gram of the peroxide placed on the charge. The material is then fused as stated.[1]

Iron and Steel. The solution of the sample, isolation of vanadium and its volumetric determination are given at the close of the chapter.

Alloys. These may be decomposed with nitric acid, or aqua regia. The isolation of vanadium with mercurous nitrate or lead acetate are given under the gravimetric methods.

SEPARATIONS

Fusion with sodium carbonate and potassium nitrate and extraction of the melt with water effect a separation of vanadium from most of the metals, which remain insoluble as carbonates or oxides. Arsenic, molybdenum, tungsten, chromium and phosphorus, however, pass into the filtrate with vanadium.

Removal of Arsenic. This element generally occurs in vanadium ores. It may be removed when desired, by acidifying the water extract of the fusion with sulphuric acid, and after reducing arsenic with SO_2, precipitating the sulphide, As_2S_3 with H_2S gas. Vanadium passes into the filtrate.

Removal of Molybdenum. The procedure is similar to that used for arsenic, with the exception that the sulphide of molybdenum is best precipitated under pressure. The solution in a pressure flask is treated with H_2S. The flask is stoppered and heated in the steam bath. It is advisable to resaturate the solution with H_2S before filtering off the sulphide.

Separation from Phosphoric Acid. In the gravimetric procedure phosphorus and vanadium are precipitated together as mercuric vanadate and phosphate. The mercury is expelled by heat and the oxides V_2O_5 and P_2O_5 weighed. (V_2O_5 in presence of P_2O_5 does not melt as it does in pure form, but only sinters.) The oxides are fused with an equal weight of sodium carbonate, the melt dissolved in water, then acidified with sulphuric acid and vanadium reduced to the vanadyl condition by SO_2 gas. The excess of SO_2 is expelled by boiling and passing in CO_2. Phosphoric acid is now precipitated with ammonium molybdate (50 cc. of a solution containing 75 grams ammonium molybdate dissolved in 500 cc. of water and poured into 500 cc. nitric acid—sp. gr. 1.2) in presence of a large amount of ammonium nitrate and a little free nitric acid. It is advisable to dissolve the precipitate in ammonia and reprecipitate in presence of additional ammonium molybdate and nitrate by acidifying with nitric acid. The equivalent P_2O_5 is deducted from the weight of the combined oxides, the difference being due to V_2O_5.

NOTE. Vanadium must be completely reduced to the vanadyl form, as vanadic acid will precipitate with phosphoric acid.

[1] Direct reduction and titration of vanadium in presence of a large accumulation of salts leads to erroneous results. The vanadium should be separated by precipitation with lead acetate.

Separation of Vanadium and Chromium. A volumetric procedure for determining vanadium and chromium in the presence of one another is given. If a separation is desired the following procedures may be used:

A. The solution is acidified with nitric acid. If hydrochloric acid is present it is expelled by taking to near dryness twice with nitric acid, the residue is taken up with water and SO_2 gas passed in to completely reduce the vanadium. This solution is poured into a boiling solution of 10% sodium hydroxide. After boiling a few minutes, the solution is filtered and the residue washed. The filtrate contains vanadium, the residue chromium. It is advisable to pour the filtrate into additional caustic to remove the small amount of chromium that passes into the solution.

B. One hundred cc. of the neutral solution is made acid with about 15 cc. of glacial acetic acid and hydrogen peroxide added. The solution is boiled for a few minutes. Chromium is thereby reduced to Cr_2O_3, whereas vanadium appears as V_2O_5. Lead acetate will now precipitate lead vanadate, the reduced chromium remaining in solution. The lead vanadate now treated with strong sulphuric acid is decomposed upon heating. Addition of water precipitates $PbSO_4$, the vanadium remaining in solution.

GRAVIMETRIC METHODS

The following procedures presuppose that vanadium is present in the solution as an alkali vanadate, the form in which it occurs in the water extract from a fusion with sodium carbonate and potassium nitrate, as is described in the method of solution of ores containing vanadium. Chromium, arsenic, phosphorus, molybdenum and tungsten, if present in the ore will be found in this solution.

Mercurous Nitrate Method for Determination of Vanadium—Gravimetric [1]

Principle. A nearly neutral solution of mercurous nitrate precipitates vanadium completely from its solution. The dried precipitate ignited forms the oxide, V_2O_5, mercury being volatilized.

Procedure. To the alkaline solution or an aliquot portion of the water extract from the sodium carbonate potassium nitrate fusion nearly neutralized with nitric acid [2] (the solution should remain slightly alkaline) is added drop by drop, a nearly neutral solution of mercurous nitrate in slight excess of that necessary to precipitate completely the vanadium present, as may be determined by allowing the precipitate to settle and adding a few drops more of the reagent. The mixture is heated to boiling and then placed on the water bath or steam plate and the gray-colored precipitate allowed to settle. The precipitate is washed several times

[1] Method of Rose.

[2] Should the alkaline solution of the vanadate be made acid, nitrous acid, from the nitrate fusion, will be liberated and cause reduction of the vanadate to the vanadyl salt, in which form it is not precipitated by mercurous nitrate; hence great care should be used in neutralizing the alkaline solution to avoid making it acid. It is a good practice to measure the acid added, having determined on an aliquot portion the amount necessary to add to neutralize the solution. This is readily accomplished when a comparatively large sample has been prepared for analysis and an aliquot portion taken for analysis, several determinations being made on the same fusion.

with water containing a few drops of mercurous nitrate, washing once or twice by decantation and finally on the filter paper. The precipitate is dried, then ignited in a porcelain crucible in a hood over a Bunsen burner to a red heat. The fused red residue is V_2O_5.

$$V_2O_5 \times 0.5604 = V.$$

Gravimetric Method of Determining Vanadium by Precipitation with Lead Acetate [1]

Principle. From a weakly acetic acid solution, vanadium is quantitatively precipitated by lead acetate. The precipitate is dissolved in nitric acid, lead removed as a sulphate, and vanadium determined in the filtrate by taking to dryness and igniting to the oxide, V_2O_5.

Procedure. To the alkaline solution or an aliquot portion obtained by extraction of the carbonate fusion of the ore with water, just sufficient amount of nitric acid is added to nearly neutralize the alkali present, as in the case of the method described for precipitation of vanadium by mercurous nitrate, and then a 10% solution of lead acetate is added in slight excess with continuous stirring. The precipitate is allowed to settle on the steam bath. The vanadate, first appearing orange colored, will fade to white upon standing. The lead vanadate is filtered and washed free of the excess of lead acetate with water containing acetic acid. The precipitate is washed into a porcelain dish with a little dilute nitric acid, and brought into solution by warming the lead salt with nitric acid. To this, the ash of the incinerated filter is added. Sufficient sulphuric acid is added to precipitate completely the lead, and the solution taken to small volume on the water bath and then to SO_3 fumes, but not to dryness. About 100 cc. of water are added and the mixture filtered; lead sulphate will remain upon the filter and the vanadium will be in solution. The lead sulphate is washed free of vanadium (i.e., until the washings no longer give a brown color with hydrogen peroxide).

The filtrate containing all the vanadium is evaporated to small volume in the porcelain dish, then transferred to a weighed platinum crucible and evaporated to dryness on the water bath and finally the residue (V_2O_5) heated to a dull redness over a Bunsen flame.

$$V_2O_5 \times 0.5604 = V.$$

NOTES. Lead may be separated from the vanadium by passing H_2S through the nitric acid solution, the excess of H_2S volatilized by boiling and the liberated sulphur filtered off. The filtrate is evaporated to dryness and the vanadium ignited with a few drops of nitric acid to the oxide V_2O_5.

Lead may also be separated as lead chloride in the presence of alcohol, the solution taken to dryness and vanadium oxidized by addition of nitric acid and ignited to V_2O_5.

[1] Method by Roscoe, Ann. Chem. Pharm., Supplement 8, 102, 1872.

VOLUMETRIC PROCEDURES FOR THE DETERMINATION OF VANADIUM

Reduction of the Vanadate, V_2O_5, to Vanadyl Condition, V_2O_4, and Reoxidation with Potassium Permanganate

Principle. Vanadium in solution as a vanadate is reduced to the vanadyl salt by H_2S or SO_2, the excess of the reducing agent expelled and the solution titrated with standard $KMnO_4$, vanadium being oxidized to its highest form, V_2O_5.

Reactions. *a.* $V_2O_5+SO_2=V_2O_4+SO_3$. *b.* $V_2O_4+O=V_2O_5$. Hence

$$N/10 \text{ sol.} = \frac{\text{At. wt. V}}{10} \text{ grams to the liter.}$$

Procedure. An aliquot portion of the solution containing vanadium, as obtained by one of the procedures given for the solution of the sample, is taken for analysis; dilute sulphuric acid (1 : 1) is added to acid reaction and 5 cc. of acid per 100 cc. of solution added in excess. The vanadium content should be not over 0.5 gram V when a tenth normal permanganate is used for the titration. *If arsenic or molybdenum is present* these may be removed from the solution by passing in H_2S. The insoluble sulphides are filtered off and washed with H_2S water. The filtrate is boiled down to two-thirds of its volume and the sulphur filtered off. In the absence of members of the H_2S group, this portion of the procedure is omitted.

Oxidation with $KMnO_4$. The solution containing the vanadium is oxidized by adding, from a burette, tenth normal potassium permanganate to a faint permanent pink. If the solution has been treated with H_2S, the vanadium is in the vanadyl condition, and the amount of permanganate required to oxidize the solution completely will give a close approximate value for the vanadium present, each cc. of N/10 $KMnO_4$ being equivalent to 0.0051 gram vanadium.

Reduction. The vanadite is now reduced to vanadyl salt by passing through the acid solution, containing approximately 5% free sulphuric acid, a steady stream of SO_2 gas. Reduction may also be accomplished by adding sodium metabisulphite, or sodium sulphite, to the acid solution. The excess SO_2 is now removed by boiling (a current of CO_2 passed into the hot solution will assist in the complete expulsion of the SO_2).

NOTE. $KMnO_4$ is reduced by SO_2.

Test for Iron. A drop test with potassium ferricyanide, $K_3Fe(CN)_6$, on a white tile will give a blue color in the presence of ferrous iron. Since ferrous iron will titrate with potassium permanganate, its oxidation is necessary. This is accomplished by adding tenth normal potassium dichromate solution cautiously to the cold liquid until no blue color is produced by the spot test with $K_3Fe(CN)_6$ outside indicator. If the sample is sufficiently dilute, the blue color of the vanadyl solution will not interfere in getting the point where the iron is completely oxidized. Care must be taken not to pass this end-point, otherwise V_2O_4 will also be oxidized and the results will be low.

NOTE. The action of the dichromate is selective to the extent that iron is first oxidized and then V_2O_4. If the amount of iron present is large a separation must be effected. In case a sodium carbonate potassium nitrate fusion has been made and

vanadium has been extracted by water, iron will not be present. A special procedure for determination of vanadium in steel is given.

Potassium Permanganate Titration. N/10 $KMnO_4$ is now cautiously added until a pink color, persisting for one minute, is obtained. During the titration the solution changes from a blue color to a green, then a yellow and finally a faint pink. The reaction towards the end is apt to be slow if made in a cold solution.

NOTES. In absence of chromium, it is better to make the titration in a hot solution, 60 to 80° C., the end-point being improved by heat. In case an excess of permanganate has been added, the excess may be determined by a back titration with tenth normal thiosulphate. The solution may be rerun, if desired, by repeating the reduction with SO_2 and the titration with $K_2Cr_2O_7$ and $KMnO_4$.

One cc. N/10 $KMnO_4$ = 0.0051 gram V, or = 0.00912 gram V_2O_5.

For solutions containing less than 0.5% vanadium a weaker permanganate reagent should be used. A fiftieth normal permanganate solution will be found to be useful for materials low in vanadium.

The author obtained excellent results by the above procedure on materials containing small amounts of iron and chromium; with amounts equal to that of vanadium present in the solution no interference was experienced. The titration with potassium permanganate is made in cold solutions if chromium is present, as the permanganate will oxidize chromium in hot solutions. Potassium permanganate added to samples containing chromic salts, and the mixture boiled, will oxidize these quantitatively to chromates. This reaction does not take place in cold solutions to any appreciable extent during a titration and only slowly in warm solutions.

Volumetric Determination of Vanadium by Reduction with Zinc to V_2O_2

The procedure proposed by Gooch and Edgar is to reduce vanadic acid, in presence of sulphuric acid, by zinc to the oxide, V_2O_2; oxidation of the unstable V_2O_2 by the air is anticipated by means of ferric chloride or sulphate, in the receiver of the Jones reductor, the highest degree of reduction being registered by the ferrous salt formed by the reaction of the reduced vanadate on the ferric salt, i.e., $V_2O_2 + 3Fe_2O_3 = 6FeO + V_2O_5$. Compounds reduced by zinc and oxidized by $KMnO_4$ must be absent or allowed for.

Procedure. The Jones reductor is set up as directed in the procedure for the determination of iron by zinc reduction. The receiver attached to the tube containing the column of zinc is charged with a solution of ferric alum in considerable excess of that required for the oxidation of the reduced vanadium. (The amalgamated zinc is cleaned by passing through the column, a dilute solution of warm sulphuric acid. The final acid washings should show no further reducing action on permanganate when the reductor is clean.)[1] Gentle suction is applied, and through the column of clean amalgamated zinc are passed in succession—100 cc. of hot water, 100 cc. of 2.5% sulphuric acid, and then the solution of vanadic acid diluted to 25 cc. in a 2.5% sulphuric acid solution, and finally 100 cc. of hot

[1] Corrections should be made for the action of zinc upon the reagents without the vanadic acids, as it is almost impossible to get a condition where no blank is obtained with permanganate. The reductor is cleaned first by passing about 500 cc. of dilute 2.5% sulphuric acid through the column of zinc. A blank is now obtained with the same quantity of reagents as is used in the regular determination, only omitting the vanadium, and this is deducted from the titration obtained for each sample reduced.

water. To the receiver is added a volume of 4 cc. of syrupy phosphoric acid to decolorize the solution. The reduced iron salt is now titrated with N/10 $KMnO_4$.

One cc. N/10 $KMnO_4$ = 0.0017 gram V, or = 0.00304 gram V_2O_5.

Determination of Vanadium in Steel

The following method is used in analyzing the Bureau's vanadium and chrome-vanadium steels. The procedure was worked out by J. R. Cain and L. F. Witmer of the U. S. Bureau of Standards.

Five to 10 grams of drillings are dissolved in hydrochloric acid (1 : 1), a few drops of hydrofluoric are added, and the solution is boiled for a few minutes. The insoluble matter is filtered off, ignited, fused with a little sodium carbonate, the fusion dissolved in water and added to the main filtrate. This is then oxidized with the minimum amount of nitric acid needed, and boiled till free from fumes. The iron is extracted with ether and the excess of ether removed from the aqueous layer by evaporation on the steam bath. After concentration on the bath, strong nitric acid is added to the solution and it is evaporated to dryness. The residue is dissolved in strong nitric acid, the solution is diluted with water and nearly neutralized with strong sodium hydroxide solution. It is then poured slowly into 150 to 200 cc. of a 10% sodium hydroxide solution, stirring vigorously. The solution is filtered, and the series of operations are repeated with the precipitate until it is free from vanadium, as shown by dissolving it in nitric acid and testing with hydrogen peroxide. In the latter treatments the amount of sodium hydroxide solution used may be smaller. From the combined filtrates the vanadium is precipitated with mercurous nitrate solution, after making nearly but not quite neutral with dilute nitric acid. After settling, the precipitate is collected on paper and washed with dilute mercurous nitrate solution. The filter is burned off in a platinum crucible and the precipitate ignited till all the mercury is expelled. The impure vanadium pentoxide left is fused with a little sodium carbonate, the fusion is dissolved in water and filtered (on asbestos) from insoluble matter. A second precipitation with mercurous nitrate is then made. Sometimes a further fusion and precipitation may be necessary in order to get a product sufficiently pure for the next step, which is a final fusion with sodium carbonate. The fusion is dissolved in dilute sulphuric acid and the vanadium is reduced by sulphur dioxide gas and titrated against N/50 permanganate after complete expulsion of the excess of reducing agent.

Volumetric Determination of Molybdenum and Vanadium in Presence of One Another

Sulphur dioxide reduces V_2O_5 to V_2O_4, but does not reduce molybdic acid provided the sample contains 1 cc. of free sulphuric acid per 50 cc. of solution and not more than 0.2 gram of molybdic acid. By means of amalgamated zinc V_2O_5 is reduced to V_2O_3 and MoO_3 to Mo_2O_3. Upon these two reactions the determination is based according to the procedure worked out by Edgar.[1] Details of the method are given in the chapter on Molybdenum, page 282.

[1] Graham, Edgar, Am. Jour. Sci. (4), 25, 332. Gooch, "Methods in Chemical Analysis," John Wiley & Sons.

Volumetric Determination of Vanadium, Arsenic or Antimony in Presence of One Another. Edgar's Method [1]

Tartaric or oxalic acid reduces V_2O_5 to V_2O_4, but does not act upon arsenic or antimony. On the other hand SO_2 causes the reduction of all three. Therefore if aliquot portions of the solution are taken, one portion being treated with tartaric acid and vanadium determined by titration with iodine, and another portion reduced with SO_2 and again titrated with iodine, the difference between the two titrations is due to the cc. of reagent required for the oxidation of the reduced arsenic or antimony.[2]

Reactions. $V_2O_4+I_2+H_2O=V_2O_5+2HI.$

$As_2O_3+V_2O_4+3I_2+3H_2O=As_2O_5+V_2O_5+6HI.$

$Sb_2O_3+V_2O_4+3I_2+3H_2O=Sb_2O_5+V_2O_5+6HI.$

Vanadium. One portion is boiled with about 2 grams of tartaric or oxalic acid, until the solution turns the characteristic blue of vanadium tetroxide. After cooling, the solution is nearly neutralized with potassium bicarbonate, and an excess of standard iodine solution added. Neutralization is now completed, an excess of bicarbonate added, and after fifteen to thirty minutes the excess iodine titrated with standard arsenious acid, starch being used as an indicator. This titration measures the vanadium present.

Arsenic or Antimony. A second portion of the solution is placed in a pressure flask and acidified with sulphuric acid. A strong solution of sulphurous acid is added, the flask closed and heated for an hour on the steam bath. After cooling, the flask is opened and the solution transferred to an Erlenmeyer flask and the excess of SO_2 removed by boiling, a current of CO_2 being passed through the liquid. The cooled solution is treated with bicarbonate, iodine added and the titration conducted exactly as described for determination of vanadium in the first portion. The difference between the first titration and the second is a measure of the cc. required for oxidation of arsenic or antimony.

Determination of Vanadium and Iron in Presence of Each Other

The solution slightly acidified with sulphuric acid is treated with sulphurous acid, the excess expelled and the reduced vanadium and iron titrated with standard potassium permanganate.[4]

$$10FeO+5V_2O_4+6H_2SO_4+4KMnO_4=5Fe_2O_3+5V_2O_5+2K_2SO_4+4MnSO_4+6H_2O.$$

The solution is now reduced with zinc in the Jones reductor and again titrated with permanganate.[3] V_2O_5 is reduced by zinc to V_2O_3, the sample being caught

[1] G. Edgar, Am. Jour. Sci. (4), **27**, 299.

[2] Gooch, "Methods of Chemical Analysis."

[3] Graham, Edgar, Am. Jour. Sci., (4), **26**, 79.

See Am. Jour. Sci., (4), **27**, 174, also Gooch, "Methods in Chemical Analysis," p. 510, for procedure determining iron, chromium and vanadium, in presence of one another.

[4] When the color has changed from a bluish-green to greenish-yellow the solution is heated to 70 to 80° C., and the permanganate titration completed in a hot solution.

in ferric alum solution (details for determining of vanadium by reduction with zinc are given under the volumetric methods for this element).

$$10FeO+5V_2O_2+12H_2SO_4+8KMnO_4=5Fe_2O_3+5V_2O_5+4K_2SO_4+8MnSO_4+12H_2O.$$

The difference between the two titrations multiplied by 0.00456 = vanadic acid (V_2O_5) originally present.

Iodometric Method for Estimation of Chromic and Vanadic Acids in Presence of One Another

The following procedure developed by Edgar,[1] is given by Gooch ("Methods of Chemical Analysis").

In carrying out the operation, the alkali salts of the chromic and vanadic acid are put into the Voit flask of the distillation apparatus shown in the cut, Fig. 71.

One or 2 grams of potassium bromide are added, the flask is connected with the absorption apparatus containing a solution of potassium iodide made alkaline with sodium carbonate or sodium hydroxide, and the whole apparatus is filled with hydrogen gas. Fifteen to 20 cc. of concentrated hydrochloric acid are added through the separatory funnel and the solution is boiled for ten minutes, an interval of time found to be enough for the completion of the reduction. A slow current of hydrogen is maintained to avoid back suction of the liquid from the Drexel bottle. The apparatus is disconnected, the Voit flask placed in a beaker containing cold water, and the alkaline solution in the absorption apparatus cooled by running water. The contents of the trap are washed into the Drexel bottle and the solution therein is made slightly acid with hydrochloric acid. The liberated iodine is titrated with approximately N/10 sodium thiosulphate and the color is brought back by a drop or two of N/10 iodine solution, after the addition of starch.

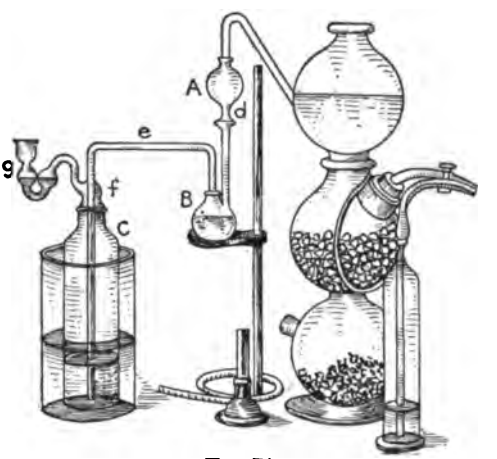


FIG. 71.

Alkaline potassium iodide is again placed in the absorption apparatus and the latter connected with the Voit flask. The current of hydrogen is turned on and, after the air has been expelled, the apparatus is disconnected momentarily, 1 or 2 grams of potassium iodide are added to the solution in the Voit flask, and connections made again. Through the separatory funnel 10 cc. to 15 cc. of concentrated hydrochloric acid and 3 cc. of syrupy phosphoric acid are added and the solution in the reduction flask is boiled to a volume of 10 cc. to 12 cc. The absorption apparatus is removed and cooled, hydrochloric acid is added and the liberated iodine titrated with approximately N/10 sodium thiosulphate.

[1] Graham Edgar, Am. Jour. Sci. (4), **26**, 333.

The iodine determined in the first titration corresponds to a reduction of the chromic and vanadic acids according to the equation

$$V_2O_5+2CrO_3+8HBr=V_2O_4+Cr_2O_3+4Br_2+4H_2O,$$

while in the second case the iodine corresponds to a reduction of the vanadium tetroxide to trioxide as indicated in the equation

$$V_2O_4+2HI=V_2O_3+I_2+H_2O.$$

The second titration, therefore, determines the vanadic acid present, and the difference between the first and second furnishes the necessary data for the calculation of the chromium.

DETERMINATION OF VANADIUM IN FERRO-VANADIUM

Standard Methods of the American Vanadium Company[1]

Dissolve 0.510 gram of the alloy (100 mesh) in a 250-cc. beaker with 50 cc. dilute sulphuric acid. (1 : 2) and 10 cc. (concentrated) nitric acid. If the alloy does not decompose, when heated, add a few cc. of hydrofluoric acid. Take down to copious white fumes. Cool, add 50 cc. dilute sulphuric acid (1 : 2) and water. Heat until all salts are in solution and transfer to a white casserole containing 100 cc. dilute sulphuric acid (1 : 2). Dilute the solution to 400 cc. with H_2O and heat to 60° C. The solution is ready to titrate.

Add potassium permanganate until a deep red is obtained. Just discharge the red color with ferrous ammonium sulphate.

Get the neutral point by alternating the permanganate and ferrous ammonium sulphate until one drop of the ferrous sulphate just discharges the pink color.

Now add N/10 ferrous ammonium sulphate from a burette until the vanadium is reduced and then 3 cc. in excess.

Titrate the excess of ferrous ammonium sulphate with N/10 potassium bichromate, using potassium ferricyanide as an indicator.

From the cc. of ferrous ammonium sulphate used, subtract the cc. of bichromate used. The number of cc. used gives the per cent of vanadium in the alloy.

The relation between ferrous ammonium sulphate and bichromate is established by adding 150 cc. sulphuric acid (1 : 2) to a casserole, diluting to 400 cc.

Find the neutral point and then add 25 cc. ferrous ammonium sulphate and titrate with bichromate until the blue spot is just discharged.

EXAMPLE

Blank.

Ferrous ammonium sulphate used	25 cc.
Potassium bichromate used	24.6 "
25.00	
24.60	
.40 ÷ 25 = −0.016 factor.	

Alloy.

Ferrous ammonium sulphate used	40.00
Potassium bichromate used	2.40
40 cc. × −0.016	= .64 cc.
40.00 − 0.64	= 39.36 "

Correction on ferrous ammonium sulphate:

39.36 − 2.4 = 36.96% V.

Solutions used:

N/10 potassium bichromate.

N/10 ferrous ammonium sulphate.

Potassium ferricyanide, a crystal the size of a pea in 50 cc. of water.

Potassium permanganate, 5 grams per liter.

[1] Methods developed in the Bridgeville Laboratory. By courtesy of the American Vanadium Company.

Determination of Vanadium in Vanadium Ores

Weigh 0.51 gram of the finely powdered ore in a 1½-in. diameter iron crucible filled three-fourths full of sodium peroxide. Fuse. Dissolve the fusion in water and add 100 cc. H_2SO_4 (1 : 2) in excess and evaporate until white fumes come off. Cool and dilute and filter. Gas the filtrate, which should be about 400 cc., until all H_2S metals are precipitated. Boil and filter. Boil the filtrate until all H_2S is off. Transfer to a 500-cc. casserole and add 50 cc. H_2SO_4 (1 : 2) and heat to above 60° C. Titrate as in the determination of vanadium in ferro-vanadium.

Determination of Vanadium in Steel

Dissolve 5.1 grams of steel in a covered 400-cc. beaker with 60 cc. of HCl (concentrated). After total solution add concentrated HNO_3 sufficient for complete oxidation. Evaporate to a syrupy consistency, add 40 cc. HCl (concentrated) and evaporate to about 20 cc. Cool and transfer contents to a separatory funnel, washing beaker with dilute HCl (2HCl : 1 H_2O).

Add 100 cc. ether, cork and shake for some time, cooling funnel under tap water while shaking. Remove cork, place funnel in stand and allow it to stand for at least five minutes. Run out the lower layer of the separation into the original 400-cc. beaker.

Evaporate the ether off. Cool and oxidize with a few crystals of sodium chlorate. Boil off the chlorine. Add 50 cc. of 1 : 2 H_2SO_4 and evaporate to copious white fumes. Cool, oxidize completely with $KMnO_4$ (5 grams to the liter), add 40 cc. of HCl (concentrated) and evaporate to dense white fumes. Cool, add 40 cc. of water, and again take down for the last time to white fumes. Cool, add 150 cc. of water, cool, and titrate with N/50 potassium permanganate. Each cc. of permanganate used is equal to 0.00102 gram of vanadium, or in this case, having used a 10-factor weight, each cc. represents 0.02% vanadium.

Determination of Vanadium in Steel (When Chromium is present)

Dissolve 5.1 grams of steel in a covered 400-cc. beaker with 60 cc. of HCl (concentrated). After total solution, add concentrated HNO_3 sufficient for complete oxidation. Evaporate to a syrupy consistency, add 40 cc. HCl (concentrated) and evaporate to about 20 cc. Cool and transfer contents to a separatory funnel, washing with dilute HCl (2 HCl : 1 H_2O). Add 100 cc. ether, cork and shake for some time, cooling funnel under tap water while shaking. Remove cork, place funnel in stand and allow it to stand for at least five minutes. Run out the lower layer of the separation into the original 400-cc. beaker.

Evaporate the ether off. Add 5 cc. HNO_3 (concentrated) and just bring to a boil, Stir out all nitrous fumes, make alkaline with NaOH (saturated solution). Make just acid with HNO_3 (concentrated) cool solution.

Add above solution to a solution containing 300 cc. cold water and 5 cc. of NaOH (saturated solution). Boil and filter, washing with hot water thoroughly. Make filtrate just acid with HNO_3 (concentrated). Add 40 cc. of a saturated solution of lead acetate. (If lead precipitate forms just clear solution by adding HNO_3 drop by drop and bring to a boil.) Add 60 cc. of ammonium acetate. Boil for twenty minutes. The vanadium is precipitated as lead vanadate.

Filter the lead vanadate onto a Munktell paper, washing with hot water. Put filter containing lead vanadate in a small porcelain dish and burn off paper at a low heat. Add a little HNO_3 and evaporate on the hot plate, then put the dish in the cold end of a muffle to drive off the remaining HNO_3. Avoid baking. Dissolve in HCl (concentrated) and transfer the solution to a 400-cc. beaker. Add 60 cc. dilute H_2SO_4 (1 : 2). Oxidize thoroughly with $KMnO_4$ (5 grams to a liter.) Add 40 cc. HCl (concentrated) and evaporate to dense white fumes. Cool, add 40 cc. of water and again take to white fumes. Cool, add 150 cc. of water, cool, and titrate with N/50 $KMnO_4$. Each cc. of permanganate used is equal to 0.00102 gram of vanadium, or in this case, having used a ten-factor weight, each cc. represents 0.02% vanadium.

Determination of Vanadium in Cupro-vanadium, Brasses and Bronzes

Dissolve 1.020 grams of cupro-vanadium in aqua regia. Evaporate to small bulk and add excess of peroxide of hydrogen. Dilute to 600 cc. and add ammonia until all copper goes into solution. Heat to boiling and add sufficient barium chloride solution to precipitate all the vanadium. Boil and filter. Wash all copper out of filter with hot ammonia water. Transfer the filter to a beaker, add 100 cc. 1 : 2 sulphuric acid, boil and filter on close filter paper. Titrate the filtrate with N/10 ferrous ammonium sulphate and N/10 potassium bichromate the same as in the case of the ferro alloy, except that this being a two-factor weight, the result must be divided by 2.

Vanadium copper, brasses and bronzes are treated in the same manner except that a ten-factor weight is used and the titration carried out with N/50 solution instead of N/10.

ZINC

F. G. Breyer.[1]

Zn, at.wt. 65.37; sp.gr. 6.48 to 7.19; m.p. 419°; b.p. 920°; ZnO oxide.

DETECTION

The finely powdered material, when heated on charcoal in the reducing flame of a blowpipe, gives an incrustation, yellow when hot—white when cold. On moistening with cobalt nitrate solution and reigniting, the mass is greenish-yellow. Materials containing above 5% Zn will give positive tests. With experience, less can be detected, but for smaller amounts the regular procedure as given under Titration in Acid Solution, Separating Zn as ZnS, should be followed, using samples as follows: For material containing 0.01–0.05%, 10 to 20 grams; 0.05–0.10%, 5 to 10 grams; 0.10–0.5%, 5 grams; 0.5% on up, 2 grams to 0.5 gram, depending on per cent of zinc present.

In case the material is of interest, only if it carries higher than several per cent of zinc, a shorter and easier wet test is to bring the material into solution by means of hydrochloric or nitric acid, add bromine water and then precipitate iron, aluminum and manganese with ammonia, as given under heading of Determination of Zinc in Acid Solution, Separating Iron, Aluminum and Manganese with Ammonia and Bromine, filter, wash and make the filtrate acid with hydrochloric acid, 10 cc. excess added for each 100 cc. of solution, and potassium ferrocyanide added. Zinc, if present, gives the characteristic precipitate. Copper interferes and if present must be separated with hydrogen sulphide, as given under heading Procedure for Copper-bearing Ores.

In case manganese and copper are known to be absent, a still shorter test may be used: To the solution of the zinciferous material add 2 or 3 grams of citric acid per 200 cc. solution, then make ammoniacal, add ferrocyanide—a white precipitate indicates zinc.

ESTIMATION

The determination of zinc is called for in the buying and selling of ores for smelters, refuse material, e.g., from galvanizing plants, foundries, brass mills, and blast furnaces, in manufacture of brass, white metals, and alloys in general, paints and pigments, zinc chloride for preservation purposes, and in the control work in smelting of zinc and lead ores.

Preliminary. The method to be followed in the estimation of zinc will depend largely on the nature of the material in which it occurs, the quantity present, and the experience of the analyst. Each of the methods outlined will give correct results only on the materials for which they are indicated, there being but one method recommended which is applicable to all zinciferous mate-

[1] In Charge of Testing Department, New Jersey Zinc Company (of Pa.), Palmerton, Pa.

rials. It cannot be emphasized too strongly that each step has a definite purpose (which may not be at once apparent to the analyst making only an occasional zinc determination), and no part of the procedure should be varied or omitted, excepting after abundant experience.

Preparation of Sample

The representative sample should be ground to pass a 100-mesh screen or finer. If the material contains shot metal, it should be screened out and the percentage present calculated. It is then treated as given under heading Material Containing Metallics, page 482.

Moisture Determination in the Pulp

One of the commonest causes of differences in zinc ore analysis is the failure to take moisture determinations on the pulp sample.

In order that analyses made on the same pulp at different times and in different laboratories may be compared it is absolutely necessary that all determinations be corrected to a dry basis. It is not sufficient that the sample be dried before or after having been pulped, but a sample for moisture must be weighed out at the same time as the sample for analysis, and the analytical result corrected for the per cent of moisture found at the time of weighing. This is especially true on roasted zinc ores which contain sulphates of zinc, iron and lime and which take up moisture quite rapidly under ordinary atmospheric conditions.

The usual temperature for drying should be 110° C., but on special ores, e.g., those containing sulphates, it is necessary to dry at 250° C. unless it is first shown that there is no loss of water above 110° C.

The determination is best made by weighing approximately two grams in a small glass-stoppered weighing tube and drying to constant weight, the weighing tube being closed with the glass stopper as soon as the tube is taken from the drying oven.

SEPARATIONS

Silica. Evaporate with hydrochloric acid or take to fumes of sulphuric acid. The dehydration with sulphuric acid is complete and gives silica that is easily filtered and washed.

Cadmium, Lead, Arsenic, Antimony, Bismuth and Copper. Aluminum may be used to separate all the metals, except cadmium, the latter being only partially separated. The procedure is as given in the standard method.

The separation may also be made as follows: Evaporate the solution of the zinciferous material to fumes with 7 cc. of 1 : 2 sulphuric acid. Cool, take up in about 50 cc. of water and warm, add 10 cc. of 10% sodium thiosulphate, boil until evolution of sulphur dioxide ceases, then filter. Cadmium if present is not precipitated. It should be separated by the procedure given under Titration in Acid Solution Separating Zinc as Sulphide.

Iron, Aluminum and Manganese. This separation may be effected by precipitation with ammonia and bromine, providing the quantities present are small. When large amounts are present the basic acetate procedure is followed, or, better, the zinc separated as sulphide in dilute sulphuric acid solution, page 485.

Nickel and Cobalt. When nickel or cobalt are present, the only safe procedure is to separate the zinc as zinc sulphide in dilute sulphuric acid solution, as described under the standard method. Weiss has shown conclusively that zinc can be precipitated free from either cobalt or nickel under the conditions there outlined.

METHODS OF ANALYSIS

I. Gravimetric methods.
II. Electrolytic methods.
III. Titration with standard solution of $K_4Fe(CN)_6$.
  (*a*) In acid solution.
  (*b*) In alkaline solution.
  (*c*) In acid solution, separating Zn as ZnS. (Standard method.)

GRAVIMETRIC METHODS

Weighing as Zinc Oxide

In this case the procedure is the same as in the volumetric method, in which zinc is separated as zinc sulphide up to point where the zinc sulphide is filtered off and washed. It is now ignited in a weighed crucible and heated to 800 to 900° C. in a muffle for one hour and weighed as ZnO. Factor $ZnO \times 0.8034 = Zn$.

The precipitate of zinc sulphide may also be filtered on a Gooch crucible, and ignited as above.

Weighing as Sulphate

The zinc sulphide is dissolved in hydrochloric acid. Sulphuric acid is added and the solution evaporated in a weighed crucible, all excess acid fumed off and the resulting zinc sulphate finally ignited at a dull red heat and weighed. $ZnSO_4 \times 0.504 = Zn$.

Electrolytic Methods

The determination is best made from an alkaline electrolyte or one slightly acid with acetic acid and containing a considerable amount of sodium acetate. The alkaline electrolyte tends to give high results, due to the presence of zinc oxide or hydroxide in the deposit. The best results are obtained with a solution weakly acid with one of the weaker organic acids. The procedure for the acetate electrolyte is as follows:

The zinc is separated from other elements by precipitating with hydrogen sulphide in dilute sulphuric acid solution, as given under the standard method. The precipitate is filtered and washed, dissolved in hot hydrochloric acid—5 cc. 1 : 1 sulphuric acid added and the whole evaporated to fumes to expel hydrochloric acid. Cool and dilute, neutralize with sodium hydrate solution, make slightly alkaline, then acidify with acetic acid, and add about 5 grams of sodium acetate. The volume of solution should now be about 100 to 125 cc. Electrolyze with a platinum gauze electrode with 0.5 ampere at 5 volts.

The electrolytic methods, on account of the special apparatus needed, the experience and care necessary to get reliable results, and the unavoidable errors involved in their use, are less desirable than the gravimetric oxide method and *still less* desirable than the ferrocyanide method.

VOLUMETRIC METHODS

Titration in Acid Solution, Separating Iron, Aluminum, and Manganese with Ammonia and Bromine

General. This method is especially adapted to material low in silica, alumina, iron, and manganese. When the operator gains experience in manipulation, it is possible to obtain good results on samples higher in these elements, but its haphazard use with materials high in these impurities is one of the chief causes of the common inaccuracy of zinc work. If copper or cadmium are present in quantities, the titration in acid solution, separating Zn as ZnS, is to be preferred for accurate work.

Procedure for Ores. One-half or 1 gram (depending on the per cent of zinc present) is weighed in a 250-cc. beaker. Fifteen cc. of hydrochloric [1] acid (sp.gr. 1.2) are added, a cover-glass put on, and the ore agitated to prevent caking. Boil down to a volume of about 5 cc.[2] cool, wash down cover-glass and sides of beaker with a jet of water. Add 10 cc. of saturated bromine water, 5 grams of ammonium chloride and 15 cc. of ammonia water (sp.gr. 0.90) and boil vigorously for a minute or two. Filter off the precipitated hydroxides, and wash four times with hot water, containing 50 grams ammonium chloride and 25 cc. ammonia per liter. The precipitate is now washed from the filter into the beaker in which the original precipitation was made, and the precipitate dissolved in strong hydrochloric acid. Ten cc. of ammonia (sp.gr. 0.9) are added, the solution boiled, filtered and washed as before, the filtrate being combined with the first filtrate.[3] The solution is then diluted to 250 cc., heated to boiling, and 4 drops of ammonium sulphide solution added to destroy oxidizing agents [4] and precipitate small amounts of copper and cadmium. The solution is neutralized with hydrochloric acid, the resolution of the precipitated zinc sulphide serving in lieu of an indicator. Ten cc. excess of concentrated hydrochloric acid are added [5] and the solution titrated, not below 75° C., with standard ferrocyanide, using uranium nitrate (10% solution)[6] as an external indicator.

Standardization of the Forrocyanide Solution

The potassium ferrocyanide is standardized by weighing out portions of C.P. zinc that will give a titration of approximately the same number of cc. as the sample. Dissolve in 15 to 20 cc. of hydrochloric acid and dilute to about 225 cc.

[1] Nitric acid should be added in case of sulphide ores.

[2] In case of siliceous ore, it is advisable to evaporate to dryness, and on unknown material to evaporate slowly, in order to make sure of complete solution of the zinc. Certain siliceous and oxide ores are difficultly soluble in hydrochloric acid, and frequently cause low results, where rapid decomposition is the routine.

[3] In case of high silica, alumina, iron, and manganese materials, three precipitations are necessary.

[4] It is necessary to destroy all oxidizing agents, as they will react with the ferrocyanide.

[5] The excess of hydrochloric acid should be carefully measured. A burette is very useful in neutralizing the solution.

[6] The strength of the uranium nitrate is a matter of personal preference, some using a saturated solution. On the other hand some prefer ammonium molybdate. The strength of solution given above, however, is recommended as the first choice of a large number of experienced zinc chemists.

Then add 37 cc. strong ammonia,[1] taking care to avoid spattering, heat to boiling, add 4 drops of ammonium sulphide, neutralize and add 10 cc. excess hydrochloric acid and titrate.

General Notes

The ferrocyanide is of the same strength as is used in titration in alkaline solution. See below.

The precipitate with ammonia carries down zinc. This is especially true with siliceous material or material high in iron and alumina. By working with hot ammoniacal ammonium chloride solution and making two or three precipitations, the amount held can usually be made negligible.

The precautions in regard to adding ferrocyanide and keeping conditions of standardization and titration the same, hold here as in all ferrocyanide titrations.

Titration in Alkaline Solution

General. This procedure is designed for rapid routine work on roasted or oxidized ores, especially those high in silica, alumina, iron, and manganese. It should only be used on unroasted sulphides, copper, or high cadmium-bearing ores, when the operator has had *long* experience. It is designed to give the zinc content of materials soluble in hydrochloric or nitric acid. For materials containing insoluble zinc, the titration in acid solution, in which zinc is separated as sulphide, is preferred.

Procedure for Common Ores. The following method is recommended: The weight of ore to be taken will depend on the approximate amount of zinc present. For material above 50%, take 1 gram; from 10 to 50%, 2 grams; 5 to 10%, 4 grams; and below 5%, 5 to 10 grams. Weigh the sample into a tall 400-cc. beaker, cover with water and add 25 cc. concentrated hydrochloric acid, rotating the beaker to prevent caking. In case sulphides are present, nitric acid also should be added. Place on a hot plate or steam bath and evaporate to dryness.[2] Now add 50 cc. concentrated nitric acid, cover with a watch crystal and boil off all nitrous fumes. When these have disappeared, add about 3 to 4 grams $KClO_3$ and boil until chlorine fumes do not show.[3] Cool, wash off the watch crystal and sides of the beaker, and dilute to about 100 cc. Wash into 500 cc. graduated flask, make up to the mark and shake well. Filter through a close 24-cm. qualitative paper and without waiting for the whole to run through, measure out 250 cc. of the clear filtrate [4] into a 600-cc. beaker. Add ferric nitrate solution, if necessary, so as to bring the iron content up to about 300 to 400 milligrams, i.e., if only a small amount is present, add 10 cc.; if 10 to 15% is present, add 5 cc., and proceed exactly as under Standardization.

Procedure for Copper-Bearing Ores. Either method is recommended:

Separation of Copper by Aluminum. The sample is treated as usual up to

[1] The amounts of acid and ammonia used throughout should be carefully measured, so as to keep the amount of ammonium salts approximately the same. This is very important in order to avoid errors, due to varying blanks.

[2] The temperature of the hot plate should not be over 120° C., as $ZnCl_2$ is appreciably volatile at higher temperatures.

[3] Any oxidizing agent such as chlorine or chlorine oxides acts on the ferrocyanide.

[4] The graduated flasks should be standardized against one another, i.e., the 500 cc. should be twice the volume of the 250 cc.

the point where manganese has been separated and 250 cc. of the clear filtrate measured out. Add 25 cc. 1 : 1 sulphuric acid and evaporate to strong fumes, cool, dilute to 100 cc., add a gram or two of 20-mesh zinc-free aluminum. Heat until all the copper separates, filter, wash and proceed with the filtrate as in the regular method.

Separation of Copper by Hydrogen Sulphide. After separation of the manganese with chlorate, sulphuric acid is added and the solution taken to fumes, as in above. Cool, dilute to 100 cc., and add sulphuric acid so that 12% is present. Warm slightly and pass hydrogen sulphide through the solution. Filter off the copper sulphide, wash, boil H_2S out of the filtrate, and titrate as usual, after adding ferric nitrate and citric acid.

Material Containing Cadmium. If the material contains cadmium in quantities sufficient to warrant separation (0.15% or more), it is best to use the titration in acid solution, separating zinc as sulphide.

Material Containing Carbonaceous Matter. If the material under examination contains carbonaceous matter, coal, etc., it must be separated by taking to dryness with hydrochloric acid. Take up in acid and water, filter and wash, and evaporate the filtrate to dryness. Take up in nitric acid and proceed as in the regular method.

If the carbonaceous material is not removed, the manganese does not separate cleanly, due to the reducing action of carbonaceous compounds.

Procedure for Material Containing Metallics. On account of the lack of uniformity in the case of metallic zinciferous material containing lead and iron, it is well to work on large samples. Five or 10 grams of the metallics reduced to as fine a size as possible are weighed out and dissolved in nitric acid. The nitrous fumes are boiled off and the whole made up to 500 cc. or 1000 cc. Fifty or 100 cc. are now pipetted off into a 600-cc. beaker and the zinc titrated as usual. In case the metallic portion contains manganese, which is unusual, it can be separated by the regular procedure. Copper is separated as given under Copper-bearing Ores. Material containing cadmium should be analyzed by other methods, as given under Standard Procedure.

Solutions. ***Potassium Ferrocyanide.*** 34.8 grams pure salt in 1000 cc. water. One cc. = approximately 0.010 Zn. This solution should be allowed to stand about four weeks before using.

Ferric Nitrate. One part salt in 6 parts water. It is well to add a little nitric acid to prevent hydrolysis.

Citric Acid. One part acid in 3 parts water. One hundred cc. of nitric acid should be added to each liter to prevent mould growth.

Standardization. The factor for the standard solution varies slightly, as would be expected, with the amount of ferrocyanide used, so that it is best to have at least three sets of factors, one at 40 cc., one at 20 cc., and one at 10 cc.

Weigh out into 600-cc. beakers at least three portions of C.P. zinc (Kahlbaum's or Merck's stick, or J. T. Baker, or Baker & Adamson 20 mesh), for each set of factors. When using 20-mesh zinc each sample should be examined under a low-power glass, for foreign matter or oxidized particles. Dissolve the metal in about 15 cc. nitric acid, first covering with water. Boil off the nitrous

fumes and dilute to 250 cc. with distilled water. Add 10 cc. of ferric nitrate solution, and 15 cc. citric acid solution, make faintly ammoniacal, using a piece of litmus paper as indicator. Then add a measured excess of ammonia, as follows: 40 cc. factor, 20 cc. excess; 20 cc. factor, 10 to 12 cc. excess; and for low titrations make only faintly ammoniacal. Heat the solution to a full boil, and titrate immediately with the standard ferrocyanide, stirring the solution *thoroughly* and adding ferrocyanide not too rapidly. The titration is completed when a drop of solution gives a bluish-green coloration with a drop of 50% acetic acid on a spot plate. To prevent passing the end-point, or until the operator is experienced, a portion (50 cc.) of the solution may be held back in a small beaker, the end-point passed, and the titration completed after adding the part in the small beaker.

General Notes

A standard zinc solution may be used in case the end-point is passed. However, this is not to be recommended as a usual practice. In any case it should be very dilute, so that 1 cc. = 0.001 gram zinc.

The ferrocyanide should be added gradually and the solution stirred constantly, to prevent occlusion of ferrocyanide or zinc solution by the heavy precipitate.

A moisture sample should be weighed at the same time as the sample for analysis.

The variation of factor with amount of zinc titrated is more marked in this method than in the titration in acid solution. Hence, it is necessary that standards be run covering the whole range of zincs to be titrated. It will be found that the factors from 30 to 50 cc. are almost the same and from 15 to 30 cc. slightly lower, from 5 to 15 cc. still lower.

The zinc used as a standard should be carefully examined for foreign particles and oxidized zinc. In case stick zinc is used, the surface should be scraped clean before cutting. Merck's and Kahlbaum's stick zinc, as well as Baker & Adamson's, Eimer & Amend's, or J. T. Baker's powdered zinc answer the purpose as regards metallic impurities. It is desirable to check the factor by means of a standard ore.

The standard of the ferrocyanide solution should be frequently checked, at least once every ten days. A solution of such a strength that 1 cc. equals 10 milligrams of zinc has in glass a temperature coefficient sufficient to decrease the factor 0.2% per 5° C. rise in temperature, so care should be taken that no sharp change of temperature occurs between standardization and titration.

The factors in alkaline and acid solution are not identical. In alkaline solution the precipitate closely approaches the normal ferrocyanide, while in acid solution there is formed a double ferrocyanide of zinc and potassium.

Standard Method

Titration in Acid Solution—Separating of Zinc as Sulphide

General. The method of separating zinc as sulphide in a solution slightly acid with sulphuric acid is of almost universal application, and can be used on any class of zinciferous material that has come under the author's observation. The steps fit together, so that copper and cadmium are easily separated and any zinc in the insoluble state, e.g., spinels, etc., can readily be looked for. The method of decomposing (taking to fumes of sulphuric acid) tends to take into solution material that would be overlooked in the rapid decompositions effected in the preceding methods. Moreover, the use of the internal indicator gives a very sharp end-point, so that this method is fully as accurate as any gravimetric method. The method is more time consuming than the ones already given, but

it is not designed for rapid routine work, but rather as a standard procedure that will give absolutely reliable results on all classes of material. This method is also recommended for routine work in case the analyst is called on to make only occasional zinc analyses.

Standardization of the Ferrocyanide Solution

NOTE. The standardization of the solution is given first, on account of the method of titration.

Weigh into tall 400-cc. beakers several portions of C.P. zinc, using about 0.35 gram. Cover with water and dissolve in 10 cc. hydrochloric acid (sp.gr. 1.2). Now add 13 cc. ammonia (sp.gr. 0.9), make acid with hydrochloric acid, and add 3 cc. excess. Add 0.03 or 0.04 milligram of ferrous iron in the form of a ferrous sulphate solution and dilute to about 200 cc. with distilled water. Heat to boiling and titrate as follows: About one-quarter of the solution is reserved in a small beaker and the ferrocyanide added to the main solution with vigorous stirring. The solution takes on a blue color, which changes to a creamy white when an excess of ferrocyanide is added. Now add a few cc. more and pour in the reserved portion of zinc solution, excepting about 5 or 10 cc. Add ferrocyanide until the end-point is reached and add about ½ cc. more. The last of the reserved zinc solution is then poured into the main beaker, washing out the small beaker with a portion of the main solution, and the ferrocyanide added drop by drop until the blue color fades sharply to a pea green with one drop of ferrocyanide.[1] This is the end-point. Repeat until satisfactory standards are obtained.

Procedure. Weigh into a tall 150-cc. beaker an amount of sample so that it gives a titration of about 40 cc., i.e., 5 grams for a 10% ore to ½ gram for 60% ore and over. Moisten with water and add 10 cc. of hydrochloric acid (sp.gr. 1.20), cover with a watch-glass. In case of sulphides it is necessary to add nitric acid. Boil moderately on a hot plate for half hour or so. Remove and wash down cover-glass and sides of beaker, add 10 cc. of 1 : 1 H_2SO_4 and evaporate to strong fumes of sulphuric acid. In case of very siliceous material, it is well to break up the silica with a glass rod before adding the sulphuric acid. After fuming, the solution is cooled and diluted to 40 to 50 cc. and about a gram of 20-mesh aluminum added. Cover with a watch crystal and boil until water white (about ten to fifteen minutes). This will reduce the iron and precipitate all the hydrogen sulphide metals, except cadmium.[2] The silica and precipitated metals are filtered off and washed with hot water.

Add 5 cc. of 1 : 1 sulphuric to the filtrate and dilute to 100 cc. Pass a rapid stream of hydrogen sulphide through the solution for fifteen minutes. Add dilute ammonia, a drop at a time until yellow cadmium sulphide precipitates. Then heat the solution to 70 to 90° C. and continue to pass hydrogen sulphide for a few minutes. Filter at once through a close paper previously packed by washing with a polysulphide, an acid and water.[3] The precipitate is washed with cold 8 to 10% sulphuric acid and finally with hot water. The filtrate is boiled to remove hydrogen sulphide, cooled, neutralized with potassium hydroxide

[1] It is only by adding an *excess* of ferrocyanide that one is assured of a precipitate of normal composition.

[2] Cadmium is partially precipitated, but goes back in solution.

[3] All the cadmium is separated, except about 0.05%, which does not interfere with the titration at the given acidity.

solution, and finally potassium carbonate solution, to within an acidity of a couple of drops of 20% sulphuric acid. Methyl orange is used as an indicator. Add from 2 to 4 cc. of 5%[1] sulphuric acid per 100 cc. of solution according to the amount of zinc present. Cool thoroughly.[2] A rapid stream of hydrogen sulphide is now passed through the solution for forty minutes.[3] Allow the precipitate to settle ten or fifteen minutes, filter and wash with cold water. A hole is punched in the filter paper and the sulphide washed back into the beaker in which it was precipitated. The filter paper and glass tube are then washed with 10 cc. of hydrochloric acid in hot water, catching the washings in the same beaker. Boil off the hydrogen sulphide, add 13 cc. of ammonia (sp.gr. 0.9), neutralize with hydrochloric acid, add 3 cc. excess and dilute to 200 cc. Heat to boiling and titrate as under Standardization. When cadmium is absent or present in quantities less than 0.05, the procedure is of course shortened considerably.

To Separate Cadmium Electrolytically. After filtering off the silica and precipitated hydrogen sulphide metals, add 1 cc. of 1 : 1 sulphuric acid, dilute to 125 cc. and electrolyze with 0.8 to 1.0 ampere per 100 sq.cm. of electrode surface for 1½ hours at 2.95 to 3.05 volts. Proceed with the residual solution as above. As in all electrolytic separations the current must be carefully watched.

Procedure with Material Containing Insoluble Zinc

Proceed as usual up to point where the solution is to be reduced. Filter off the silica and insoluble material, wash with hot water and proceed with the filtrate as usual. Burn the insoluble residue in a platinum crucible, taking the usual precautions in case lead is present. Fume off the silica with hydrofluoric and sulphuric acids and fuse with acid potassium sulphate. Dissolve in water and sulphuric acid and proceed as in the regular method. The solution may be added to the main portion or analyzed separately.

Discussion on Separating Zinc as Zinc Sulphide and Titrating in Acid Solution

Precipitation. The method of precipitating zinc as sulphide in sulphuric acid solution was investigated by G. Weiss (Inaugural Dissertation, München, 1906), and the work confirmed by the author. The main points of Weiss' paper are as follows:

1. "Sulphate solutions are preferable to chlorides." A N/10 chloride solution is not completely precipitated by H_2S. Furthermore, the precipitate of sulphide from HCl solution when quantitative is not crystalline and easy to filter like that obtained from sulphate solution.

2. "The concentration of a sulphate solution is without influence on the completeness of precipitation from N/10 down. That is for solutions containing at most 400 milligrams ZnO per 100 cc."

3. "Sulphate solutions of 400 milligrams ZnO per 100 cc. may be N/100 acid with H_2SO_4 before beginning the precipitation." Even at acidity N/20 before

[1] Bear in mind at this point the acid liberated by the action of H_2S in the zinc sulphate. See Discussion below.

[2] In cold solution the precipitate is more granular and easier to filter.

[3] The hydrogen sulphide should pass through at a rate of at least eight bubbles per second.

precipitation less than a milligram of zinc remains unprecipitated. According to Weiss, if the solution were diluted to 300 cc. 1.3 grams of H_2SO_4 could be added or 6½ cc. of 20% H_2SO_4, and still have the precipitation complete. Even if as much as 10 cc. of 20% acid were added the loss would still be only a little more than 1 milligram. Precipitating 300 milligrams from 100 cc., however, only 100 milligrams or ½ cc. of 20% acid could be added. This means that when the solution becomes more acid than 550 milligrams of H_2SO_4 per 100 cc. the precipitation of ZnS ceases. Knowing approximately the zinc content of a solution one can easily calculate the H_2SO_4, freed when the $ZnSO_4$ is converted into ZnS, and the difference between 550 milligrams and this calculated H_2SO_4 is the amount of acid that may be added when precipitating from 100 cc. of solution. For two hundred cc. of course more acid can be added, being the difference between 1.100 grams and the calculated H_2SO_4 freed from the $ZnSO_4$. One and one-half times the amount of Zn judged to be present is close enough for the H_2SO_4 freed.

4. "The precipitation, under the above given conditions, is incomplete when a slow current of hydrogen sulphide is used (about four bubbles per second). One must work with as fast a stream as possible without causing mechanical losses (at least eight bubbles per second)." Weiss is the first one to discuss this all-important question in the precipitation of ZnS. His explanation of the efficacy of the rapid stream of H_2S is as follows:

The precipitation takes place according to the following equation:

$$ZnSO_4 + H_2S \leftrightarrows ZnS + H_2SO_4.$$

Equilibrium is reached, i.e., the velocity becomes equal in both directions, and precipitation ceases when the amount of H_2SO_4 per 100 cc. reaches a certain point, under a given set of conditions. Let these conditions remain exactly the same with the exception of the H_2S and have the active mass of that increased. The equilibrium will be displaced from left to right and as a consequence ZnS will come down in the presence of more acid than before. H_2S is not very soluble in water at room temperature, but if one increases the surface of contact between the two the H_2S is dissolved much more rapidly and consequently the mass of H_2S active at any time greatly increased. This is exactly what is accomplished when the zinc solution is constantly kept full of bubbles of H_2S. One can easily see how greatly increased the mass of H_2S would be in the extreme case, when the solution is all foam.

5. "A strong current of gas, like that called for above, will precipitate the usual amounts of zinc used in analytical operations in forty minutes."

6. "At temperatures above 50° the precipitation is incomplete; furthermore, at room temperature the ZnS comes down in a form suitable for filtration."

Weiss found that not only were the precipitations incomplete at high temperatures, but the precipitate was finer and much more difficult to filter.

7. "Water only is required for washing the precipitates."

End-point. The change of color from blue to pea green is very sharp. It should be observed by looking down through the solution and not from the side. The change in color may be explained as follows: The ferrocyanide, having stood for three or four weeks, has oxidized slightly to ferricyanide, due to dissolved oxygen in the water. The few tenths of a milligram of ferrous iron added acts with this ferricyanide giving the ferro-ferricyanide blue as long as the ferro-

cyanide is not in excess. When it is in excess the blue is decomposed and gives the colorless ferro-ferricyanide.

In case the ferrocyanide solution is freshly prepared, it is well to add about 300 milligrams of ferricyanide to each liter.

DETERMINATION OF SMALL AMOUNTS OF ZINC

The following method is applicable to samples containing 0.05% Zn or less.

Procedure. A large sample, 10 or 20 grams, is brought into solution by the standard procedure, taken to fumes of sulphuric acid and the zinc precipitated as sulphide after separating groups 5 and 6 by the procedures given under Standard Method, filtered and dissolved in hydrochloric acid. The sample is now washed into a 100-cc. Nessler tube, 5 cc. of ferrocyanide added and the whole made up to the mark, mixed by pouring into a beaker and then back into the tube. A standard containing the same amount of acid is made up and a standard zinc chloride solution added until the turbidity of standard and unknown are the same. From the amount of zinc added to the standard the percentage can be calculated. The standard zinc solution is made up by dissolving C.P. zinc in hydrochloric acid and diluting so that 1 cc. is equal to 1 milligram of zinc.

SPECIAL METHODS

Determination of Metallic Zinc in Zinc Dust

Discussion. From time to time, there have been proposed various methods for determining the metallic content of zinc dust. Most of these are based on the measure of its reducing power, for example, on potassium bichromate, iodate, ferric sulphate and the like. However, none of these gives as consistently accurate results as the hydrogen evolution method. The apparatus described below was proposed by Franz Meyer in 1894, and the method thoroughly investigated by Morse and Barnes, de Koninck and Grandry. Their conclusions as to its accuracy have been confirmed by the author.

The methods based on the precipitation of a metal, for example, silver from a solution of silver cyanide in potassium cyanide, while they may give information as to the efficiency of the zinc dust under certain conditions, such as in cyanide work, they do not give the metallic zinc content.

The determination is best made by measuring the volume of hydrogen evolved when the sample is treated with dilute sulphuric acid.

The apparatus, which is similar to a nitrometer, consists of a graduated tube 72 cm. long, having a bulb at the top capable of holding 260 cc., the total capacity of the bulb and tube being 400 cc. The tube is graduated in 0.25 cc. By means of ground-glass joints connection is made with a special three-way stop-cock and a decomposing flask with a capacity of 350 cc. The stop-cock is special in that, while it resembles an ordinary three-way cock in every other respect, it has an extra hole at right angles to and connecting with the opening leading to a leveling bottle. Fig. 72 gives a sketch of the apparatus.

Procedure. One gram of zinc dust is rapidly weighed and transferred to the dry decomposing flask.[1] Approximately 5 grams of C.P. ferrous sulphate

[1] The sample should be weighed rapidly, and the flask be perfectly dry, on account of the ease with which the finely divided zinc oxidizes.

and a piece of platinum about 2 cm. square are placed in the flask.[1] Water is n added almost up to the neck, the connection holding the stop-cock is put place and the flask completely filled with water. The connection is now m with the measuring tube and the stop-cock turned to position 1 (Fig. 73).

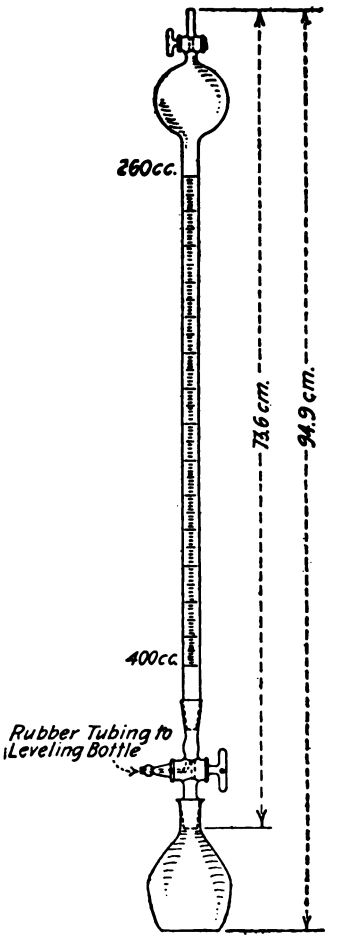


Fig. 72.

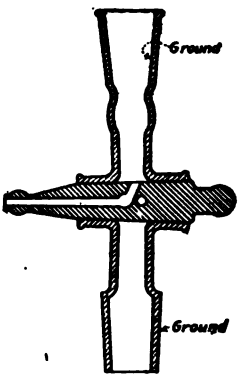


Fig. 73.

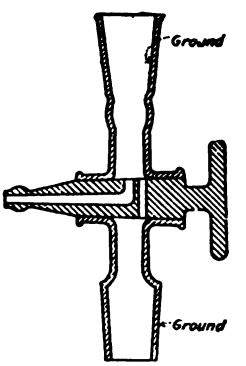


Fig. 74.

means of the leveling bottle the tube is filled with dilute sulphuric acid (1 : 10 The stop-cock is now turned to position 2 (Fig. 74). The acid descends into th flask, and the evolved hydrogen passes up into the measuring tube. The app ratus is shaken from time to time, but care should be taken not to allow a t vigorous evolution of gas.

[1] The ferrous sulphate and platinum act as catalytic agents, increasing the ra of evolution of hydrogen.

When all the hydrogen is evolved, which takes from two to twelve hours, depending on the composition of the zinc dust,[1] the volume is measured, temperature and pressure taken, and the volume reduced to 0° and 760 mm. The volume of hydrogen is calculated to zinc by multiplying by the factor 0.2914 and dividing by a factor to correct for the solubility of hydrogen in 1 : 10 sulphuric acid. This factor is determined by running samples of C.P. zinc. The sulphuric acid can be saturated with hydrogen before using, in which case the correction factor can be made negligible.[2]

DETERMINATION OF IMPURITIES IN SPELTER

LEAD

Electrolytic Method. The sample is thoroughly mixed on a sheet of paper, and pieces showing discoloration are discarded.[3] The pieces are removed from the paper by lifting, not pouring. A magnet is passed over the sample to remove particles of iron.

8.643 grams[4] are weighed into a 250-cc. beaker, about 100 cc. of distilled water added, and 40 cc. of concentrated nitric acid added gradually until solution is complete. The solution is boiled to expel all nitrous fumes and diluted to 200 cc. with distilled water, 4 or 5 drops of 5% silver nitrate added to precipitate any traces of chlorine present, and the solution electrolyzed hot. For samples low in lead, as high grade,[5] a current of 0.25 ampere is used, and for intermediate, brass special and prime western, 0.50 ampere. The anode is made of sheet platinum and is sand blasted. It has a surface of 135 sq.cm. A spiral of platinum wire is used as a cathode. The time required is from one and one-half to two hours. The solutions are tested for lead before shutting off the current, by raising the liquid in the beaker, allowing to continue for twenty minutes and if there is no fresh deposit, the anode is washed three times with

[1] It is a well-known fact that very pure zinc is only slowly dissolved by sulphuric acid.

[2] If the sample contains iron in sufficient quantity to influence the result, a correction should be made.

[3] The sample should be taken by pouring the molten metal into water, thus granulating it, or by sawing or drilling the slabs. In this latter case the slabs should be sawed or drilled completely through. No lubricant should be used. The sample is then washed with water, dried and run under a magnet.

[4] This is an empirical factor weight, 0.866 being the theoretical factor to convert the dioxide to lead. See E. F. Smith, Electroanalysis.

[5] The rejection limits for spelter of the American Society for Testing Materials consider four grades as follows:

Designation.	Proportion of Lead.	Proportion of Iron.	Proportion of Cadmium.	Total Proportion of Impurities.
A or high grade	0.07	0.03	0.05	0.10
B or intermediate	0.20	0.03	0.05	0.50
C or brass special	0.75	0.04	0.75	1.20
D or prime western	1.50	0.08		

Each grade should be free of aluminum.

distilled water, and once with alcohol, dried in the air bath at 210° C. for one-half hour and weighed.

The weight of PbO_2 found (in milligrams) divided by 100 gives the percentage of lead.

"Lead Acid" Method. Add 1 gram of lead acetate in 300 cc. of water to dilute sulphuric acid (300 cc. acid to 1800 cc. of water). Shake well, allow to cool and settle. Filter off the precipitated lead sulphate. By the use of this sulphuric acid saturated with lead, the solubility of lead sulphate need not be considered, the solution being brought back to the same concentration each time.

Procedure. Weigh 10 grams of the sample into a 400-cc. beaker and add 120 cc. of "lead acid.". When all but about 10% of the zinc is dissolved, filter and wash with lead acid. Retain the filtrate. Wash the metallics back into the beaker and dissolve in nitric acid. Add 40 cc. of "lead acid" and evaporate to strong fumes. Cool and add 35 cc. of water, which is the amount evaporated from the "lead acid," and heat to boiling. Add the filtrate containing most of the zinc and a little lead sulphate, stir and allow to settle over night. Filter on a Gooch crucible, wash with lead acid, a mixture of alcohol and water (1 : 1), finally with alcohol and ignite inside a porcelain crucible and weigh as lead sulphate.

IRON

Hydrogen Sulphide Method. Weigh 10 grams of sample which has had any metallic iron particles or iron containing dust removed with a magnet. Place in a 250-cc. beaker, and dissolve with 50 cc. concentrated hydrochloric acid. Let stand several minutes until violent action has ceased, then add about 1 cc. potassium chlorate solution (50 grams per liter), and boil until the chlorate is all decomposed. Cool, add 50 cc. of water and neutralize the solution with ammonia, adding a large excess, boil for two or three minutes, allow the precipitate to settle, filter and wash with hot dilute ammonia water and finally with hot water. Dissolve the precipitated hydroxide of iron into a 16-ounce Erlenmeyer flask, using 10 cc. dilute sulphuric acid (1 : 4). Wash the paper thoroughly with hot water, dilute to a volume of about 300 cc. and reduce the iron by passing hydrogen sulphide through the solution for five minutes, boil to expel excess of hydrogen sulphide, being careful to exclude the air by means of a Bunsen valve. Test for hydrogen sulphide with a piece of moistened lead acetate paper. Cool rapidly and titrate with permanganate, 1 cc. of which is equal to approximately 0.00034 gram of iron. Run a blank determination in order to determine the amount of permanganate necessary to show the pink color on titration. Standardize the permanganate against sodium oxalate. (Bureau of Standards.)

Colorimetric Method

Solutions. ***Ammonium Sulphocyanate.*** One part salt to 2 parts of water. ***Potassium Chlorate.*** One part salt to 20 parts of water.

Standard Iron Solution I. One to 50 grams of granulated zinc of low iron content are dissolved in 800 to 1000 cc. of hydrochloric acid and oxidized with potassium chlorate. The solution is boiled to expel chlorine fumes, and made up to 2500 cc. This solution is standardized by measuring off 50-cc. portions, corresponding to 10 grams of zinc, and determining the iron content by the hydrogen sulphide method.

Standard Iron Solution II. 0.7 gram of ferrous ammonium sulphate is dissolved in water, 10 cc. dilute sulphuric acid added, and the iron oxidized with permanganate. The solution is now diluted to 1000 cc. One cc. equals 0.0001 gram iron.

Procedure. Ten grams of sample are dissolved and oxidized as given under the hydrogen sulphide method. The solution is cooled and diluted to about 25 cc. and transferred to a comparison tube,[1] 2 cc. of the sulphocyanate solution are added, and the volume brought up to 100 cc. and mixed by pouring into the beaker and back into the tube. Compare the red color with the color produced on adding 2 cc. of sulphocyanate to 50 cc. of standard iron solution I,[2] and diluting to 100 cc. Add standard iron solution II until the colors are the same, and calculate the iron present in the unknown. In case the iron is over 0.030, it should be determined by the hydrogen sulphide method.

CADMIUM

Sulphide Method. Twenty-five or 50 grams are weighed in a liter flask, 200 cc. water are added followed by 25 cc. of (1 : 1) sulphuric acid. (In case of high-grade spelter, add a piece of platinum to accelerate the action.) Add more acid from time to time, or, if the action is too violent, add water.[3] When the greater part of the zinc is in solution, filter off the metallics, leaving the greater portion in the flask, and wash with hot water. Wash the metallics on the filter paper back into the flask, add nitric acid and heat until all is in solution, then add 25 cc. (1 : 1) sulphuric acid and take down to dense white fumes and cool. Carefully add water and heat until soluble salts are in solution, allow to cool and let the $PbSO_4$ settle. Filter and wash, dilute to 200 cc. and pass hydrogen sulphide through the solution fifteen or twenty minutes, then add a few drops (4 to 5) of ammonia and pass hydrogen sulphide about ten minutes more. If no precipitate appears, add a drop or two more of ammonia and repeat in about five minutes. Continue until a precipitate of CdS and ZnS is obtained. Filter, wash with cold water, and dissolve in (1 : 1) hydrochloric acid, wash and add 12 to 15 cc. of 1 : 1 sulphuric acid and evaporate to fumes, dilute to 100 cc. and pass hydrogen sulphide. Add ammonia as before but not so much at a time. Finally, 1 or 2 drops will give a clean yellow precipitate. In case a large amount of cadmium is present, a third precipitation is necessary. (This is usually desirable in any case.) Filter at once on a weighed Gooch, wash with cold water, alcohol, carbon bisulphide and alcohol. Dry at 110°, and weigh as cadmium sulphide.

The cadmium may also be weighed as cadmium sulphate or as phosphate.

Electrolytic Method. The same procedure is followed as given in the preceding method. After the lead sulphate is filtered off, enough water is added to make the sulphuric acid content 5 to 7%; about 5 grams of potassium sulphate are then added and the solution electrolyzed for an hour to an hour and a half with 0.20 to 0.35 ampere at 2.75 volts at the beginning to 2.95 to 3

[1] Clear glass test-tubes ¾ in. in diameter, and holding 110 cc. make good comparison tubes.

[2] The zinc content of the standard and unknown must be approximately the same. (See references, Bureau of Standards Bulletin.)

[3] Care should be taken that the solution does not proceed too rapidly. The metallics should contain about 5% of zinc.

volts at the end. The electrode is of platinum and is coated with cadmium.[1] It has a surface of 75 sq.cm.

The cathode is washed three times with water, dipped into alcohol and burned off carefully, or it may be dipped into ether and dried in an oven.

Discussion. Lead can be more rapidly determined by using higher currents, e.g., up to 5 amperes, by rotating the electrode, or by means of the solenoid of Frary.[2] However, where a great number of determinations are made, the slower electrolysis is to be preferred.

In cases where only an occasional analysis is made, the lead acid method should be used.

Determination of Impurities in Zinc Oxide

See chapter on analysis of paint pigments, page 627.

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ZIRCONIUM

R. STUART OWENS.[1]

Zr, *at.wt.* 90.6; *sp.gr.* 4.15; *m.p.* 1700° ± C.; *oxides* ZrO_2, ZrO_3.

DETECTION

The zirconium having been brought into solution by one of the methods outlined below may be distinguished:

(1) By the addition of sodium phosphate to a slightly acid solution. A white precipitate which is difficultly soluble in hydrochloric acid is characteristic of zirconium.

(2) By its solution in hydrochloric acid coloring turmeric paper orange. Titanium, however, colors it brown, and is apt to mask the color due to titanium when both are present, hence it is necessary to reduce the titanium by the addition of a few pieces of zinc. Reduced titanium does not color turmeric paper, but it oxidizes rapidly, hence the test should be made as quickly as possible. Boric acid also produces a yellow color with turmeric paper, but both elements are met with in the same sample on very rare occasions only.

(3) From alumina by the solubility of its carbonate in an excess of an alkali carbonate. The solution from ammonium carbonate if boiled precipitates zirconia.

(4) From glucinum by the insolubility of its hydroxide in ammonium chloride. Glucinum hydroxide dissolves readily in the reagent.

(5) By spectroscopic methods. Zirconium shows lines of greatest intensity in the arc spectrum at 4687.9, 4739.6, 4772.5, 4815.8, and in the spark spectrum at 3999.1, 4149.4, 4209.4, 4380.1.[2]

ESTIMATION

The determination of zirconium is required in minerals, artificial gems, incandescent gaslight mantles, firebrick, enamels, glass and various salts of the mineral acids. The chief source of zirconium is the mineral zircon ($ZrSiO_4$) and its valuable modifications as hyacinth. Zircon contains from 60 to 67% of ZrO_2.

Preparation and Solution of the Sample

A. Materials Containing a Large Amount of Silica

Decomposition by Hydrofluoric Acid. Five grams of the finely powdered sample are treated in a large platinum dish with 50 cc. HF and 50 cc. of H_2SO_4. When the violent action has ceased the solution is evaporated first on the steam bath to expel the HF and then on a sand bath till fumes of SO_3 are given off. The

[1] Research Chemist, New York City.

[2] All of these lines are in the visible spectrum.

residue is taken up with water. This usually effects complete solution of the sample. If, however, an insoluble residue still remains, it is filtered off, washed with cold water, ignited in platinum, and fused with 10 parts by weight of potassium acid sulphate. The cooled fusion is dissolved by boiling with 20% HCl. All the zirconium will now be in solution and may be determined as detailed below. Barium if present will remain insoluble and should be filtered off.

NOTES. Heating the mineral to dull redness and suddenly plunging into cold water enables zircon to be easily pulverized.

If the $KHSO_4$ fusion is extracted with dilute H_2SO_4 and boiled, the white basic sulphate, $3ZrO_2 \cdot SO_3$, is apt to form and remain in the residue.

B. General Method for Minerals, Oxides, etc.

Decomposition by Fusion with an Alkali Carbonate. Two grams of the finely pulverized sample are fused with 10 grams of Na_2CO_3 (free of sulphur) and ½ gram of KNO_3 in a large platinum dish.[1] The melt is taken up in water and if manganese is present a few drops of alcohol are added to reduce the manganate to the manganous condition. The solution is filtered and the residue washed with dilute NaOH solution. The filtrate then contains all the silica as sodium silicate, while the residue contains all the zirconium, barium, etc. The residue is dissolved in dilute H_2SO_4 and the zirconium present determined as detailed below.

C. Other Methods of Decomposition which are Sometimes Used

Fusion with acid potassium fluoride.

Fusion with caustic soda and sodium fluoride.

By long boiling with concentrated hydrochloric acid.

SEPARATIONS

From Iron by the volatilization of the iron as chloride in the presence of strong hydrochloric acid and chlorine at a temperature of 200 to 300° C.[2]

From Iron. Zirconium is precipitated free from iron by phenylhydrazine.[3]

From Titanium by precipitating the titanium from dilute sulphuric acid solution by boiling in the presence of acetic acid.[4]

From thorium by precipitation of both metals as oxalates by ammonium oxalate and then adding an excess of oxalic acid when the zirconium oxalate dissolves completely.[5]

From cerium and the iron groups by boiling the hydrochloric acid solution with sodium thiosulphate. The zirconium is precipitated as thiosulphate, which may, after filtering and washing, be ignited to the oxide.[6]

Tartaric acid prevents the precipitation of zirconium hydroxide.

[1] A nickel dish should be used in place of platinum if sulphur, lead or phosphorus is present.

[2] Havens and Way, A. J. C., (4), 7, 217.

[3] Allen, J. A. C. S., 25, 426.

[4] Streit and Franz, J. pr. Chem., 108, 75; Streit and Franz, Zeitsch, anal. chem., 9, 388.

[5] Roscoe and Schorlemmeyer, Vol. II, Part II, p. 276.

[6] Ibid., p. 272.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ZIRCONIUM

Salts of Zirconium

"A" solutions containing zirconium are treated with 5 cc. of H_2SO_4 and evaporated to fumes; taken up with cold water and diluted to 400 cc.

"B" dry salts are treated with 5 cc. of H_2SO_4 and heated to fumes of SO_3 on a sand bath. The residue is taken up with cold water and diluted.

Minerals, Silicates, etc.

The sample having been decomposed by one of the methods outlined and the zirconium being present in solution as sulphate the liquid is diluted so as to contain about 1% of free H_2SO_4.

Determination as Phosphate

To the acid solution sufficient H_2O_2 is added to oxidize the titanium which may be present. (The solution is colored yellow by H_2O_2 when titanium is present.) A sufficient quantity of ortho-phosphate (as $(NH_4)_2HPO_4$ or Na_2HPO_4) is added to precipitate all the zirconium as phosphate (aluminum and iron are not precipitated in the presence of free acid). If titanium is present and the color bleaches after a time, more H_2O_2 is added until the color is restored. (Any reduced titanium is carried down with the zirconium phosphate.) The precipitate is filtered off, washed well with water containing some H_2O_2, ignited and weighed as zirconium phosphate, which contains 51.8% of ZrO_2. The solution after precipitation should be allowed to stand several hours. Traces require ten to fifteen hours, while considerable amounts of zirconium require only from thirty minutes to one hour of settling on the steam bath for complete precipitation.

Determination as Zirconium Oxide

With pure salts the zirconium may be precipitated completely as the hydroxide by the addition of ammonia, settling and finally igniting and weighing as the oxide, ZrO_2.

Determination as Zirconium Oxide in the Presence of Iron Oxide[1]

The aqueous solution of zirconium and iron free from other metals is treated with a slight excess of ammonia water and then boiled to remove the excess. The precipitated hydroxides are filtered off, washed with water, and dried at 105° C. The filtrate is evaporated to dryness, the residue taken up in hydrochloric acid and the solution again precipitated as before. The combined precipitates which have been dried to constant weight in a porcelain crucible are cooled and weighed as $ZrO_2 \cdot Fe_2O_3$. The oxides are then ground in a mortar, weighed into a platinum crucible and ignited to constant weight in a current of hydrogen. Only the iron is reduced to the metallic state, hence data are at hand for calculating the percentages of iron and zirconium.

[1] Method of Gutbier and Hüller, Zeit. anorg. Chem., **32**, 92.

PART II

SPECIAL SUBJECTS

ACIDS

WILFRED W. SCOTT

To determine the amount of free acid present in a given solution, an alkaline reagent of known strength is required, since acids are most accurately estimated by titration. Under certain conditions, not only the free acid but also the combined is determined by titration, e.g., H_2SO_4 in $Al_2(SO_4)_3$, (see Aluminum), when caustic is added to a hot solution with phenolphthalein as indicator. When an equivalent amount of caustic has been added to the acid present the solution becomes neutral, a condition spoken of as the "end-point," which is recognized by means of certain compounds known as indicators. The accuracy of the results depends largely upon the choice of the indicator used.

INDICATORS

Indicators are usually dyestuffs, or organic compounds, which impart a different color to an acid solution than to one which is alkaline. This color is attributed to a particular arrangement of atoms in the compound called a chromophor. It is thought that the change of color is caused by a slight rearrangement of the atoms in the molecule, or is due to the fact that in certain cases the ions have a different color from the undissociated molecules. A large number of indicators are known, but for general purposes the following will cover the requirement of acidimetry and alkalimetry—methyl orange, methyl red, phenolphthalein, litmus, lacmoid.

INDICATOR	CONDITION OF SOLUTION	GENERAL USE IN TITRATION
Methyl orange. acids = red alkalies = yellow.	Cold solution only.	Hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, borates of sodium potassium, ammonium, calcium, magnesium, barium, etc.
Methyl red. As above.	Cold solution only.	Especially adapted for titration of weak bases such as NH_4OH.
Phenolphthalein. acids = colorless alkalies = red.	Cold solutions.	Alkaline hydrates, the mineral acids, organic acids, e.g., oxalic, citric, tartaric, acetic. The indicator very sensitive to acids and adapted to titration of weak acids —carbonic acid, etc.
	Hot solutions.	The indicator is sensitive in hot solutions to the above. It is generally used in hot solutions for titration of acids combined with comparatively weak bases.

Indicator	Condition of Solution	General Use in Titration
Litmus. acids = red alkalies = blue.	Cold solutions.	Hydrates of Na, K, NH_3, Ca, Ba, etc. Silicates and arsenates of Na and K, HNO_3, H_2SO_4, HCl and $H_2C_2O_4$.
	Hot solutions.	In addition to above neutral and acid carbonates of K, Na, Mg; the sulphides and silicates of Na, K.
Lacmoid. In alcohol acids = red alkalies = blue.	Cold solutions.	The alkaline and alkaline earth hydrates, the arsenates, borates, mineral acids, many salts of metals which are acid to litmus and neutral to lacmoid, e.g., sulphates and chlorides of iron, copper and zinc, hence of value in determining free acids in their presence.
	Hot solutions.	In addition to the above, carbonates and bicarbonates of K, Na, Ca, Sr, Ba, etc.

In general, methyl orange, methyl red and lacmoid are especially sensitive to bases, but not so sensitive to acids and are not used for weak acids. Phenolphthalein is especially sensitive to acids and is of value in titrating weak acids. Litmus is commonly used as a test indicator (litmus paper) though with careful preparation, it is valuable for general acid and alkali titration.

The following table compiled by Thomson,[1] refers to the number of atoms of hydrogen displaced by monatomic metals, such as sodium or potassium in solution as hydroxides.[1]

Acids		Methyl Orange Cold	Phenolphthalein		Litmus	
Name	Formula		Cold	Hot	Cold	Hot
Sulphuric	H_2SO_4	2	2	2	2	2
Hydrochloric	HCl	1	1	1	1	1
Nitric	HNO_3	1	1	1	1	1
Thiosulphuric	.....	2	2	2	2	2
Carbonic	H_2CO_3	0	1 dil.	0	.....	0
Sulphurous	H_2SO_3	1	2	....	.....	....
Hydrosulphuric	.....	0	1 dil.	0	.....	0
Phosphoric	H_3PO_4	1	2	....	.....	....
Arsenic	H_3AsO_4	1	2	....	.....	....
Arsenious	H_3AsO_3	0	....	....	0	0
Nitrous	HNO_2	indicator destroyed	1	....	1	....
Silicic	H_4SiO_4	0	....	....	0	0
Boric	H_3BO_3	0	....	....	.....	....
Chromic	H_2CrO_4	1	2	2	.....	....
Oxalic	$H_2C_2O_4$	.....	2	2	2	2
Acetic	$HC_2H_3O_2$	.....	1	....	1 nearly	....
Butyric	$HC_4H_7O_2$	.....	1	....	1 nearly	....
Succinic	$H_2C_4H_4O_4$	.....	2	....	2	....
Lactic	$HC_3H_5O_3$	.....	1	....	1	....
Tartaric	$H_2C_4H_4O_6$	.....	2	....	2	....
Citric	$H_3C_6H_5O_7$	.....	3	....	.....	....

[1] Volumetric Analysis, Sutton, Tenth Edition, page 44. R. T. Thomson, J.S.C., 1., 12, 432.

In general, the acid in the indicator must be weaker than the acid which it is required to determine by its means. Methyl-orange, for example, is a fairly strong acid, hence it is not used for titration of organic acids as the end reaction is uncertain; it is not sensitive to carbonic, hydrocyanic, boric, oleic acids; on the other hand, phenolphthalein, being an extremely weak acid, is decomposed by organic acids, H_2CO_3, etc., hence is of value in determination of these acids.

ULTIMATE STANDARDS

Sulphuric and hydrochloric acids are generally used as the ultimate standard acids. Benzoic acid may also be used.

Sodium carbonate is the best of the alkali standards. This salt may be prepared in exceedingly pure form. It is frequently used as the basic material for the volumetric standardization of the standard acid.

Preparation of Pure Sodium Carbonate

Bicarbonate of Soda made by the Ammonia-Soda process may be obtained in exceedingly pure form. The impurities that may be present are silica, ammonia, lime, arsenic, sodium chloride and sodium sulphate. With the exception of silica and lime the impurities may be readily removed by washing the bicarbonate of soda several times with cold water and decanting off the supernatant solution of each washing from the difficultly soluble bicarbonate. The washing is continued until the material is free from chlorine, as sodium chloride is the principal impurity, and its removal leaves an exceedingly pure product. The bicarbonate is dried between large filter papers in the hot air oven (100° C.).

Standard Sodium Carbonate is made from this pure sodium bicarbonate by heating at 290° C. to 300° C. in an electric oven. If a constant-temperature oven is not available a simple oven may be improvised by use of a sand bath and a large beaker or a sheet-iron cylinder covered at the upper end as shown in Fig. 75. A thermometer passing through this shield registers the temperature of the material, within a large platinum crucible. This crucible rests upon a triangle, so that the bicarbonate is entirely surrounded by an atmosphere of comparatively even temperature.

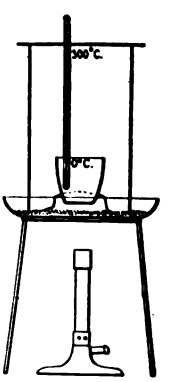

FIG 75.

The sodium bicarbonate is converted to the carbonate. Constant weight will be obtained in about five or six hours. When the material no longer loses weight it is cooled in a desiccator and bottled for use, preferably in several small, glass-stoppered bottles. For exceedingly accurate work the material is analyzed and allowance made for the impurities that may still remain. The error caused by any such impurities is so small that for all practical purposes it may be neglected.

This purified sodium carbonate is the ultimate standard for acidimetric and alkalimetric volumetric analysis.

PREPARATION OF STANDARD ACID

Standard Sulphuric Acid

Fifty-two per cent sulphuric acid is in equilibrium with the average moisture present in the air of the laboratory; acid of this concentration is recommended for the standard stock solution.[1]

Pure 94 to 97% H_2SO_4 is diluted with sufficient water so that its gravity is

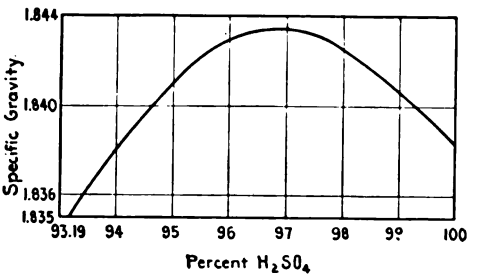

FIG. 76.

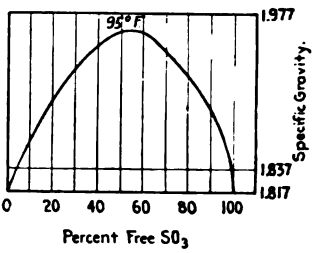

FIG. 77.

Specific Gravity Charts—Sulphuric Acid.

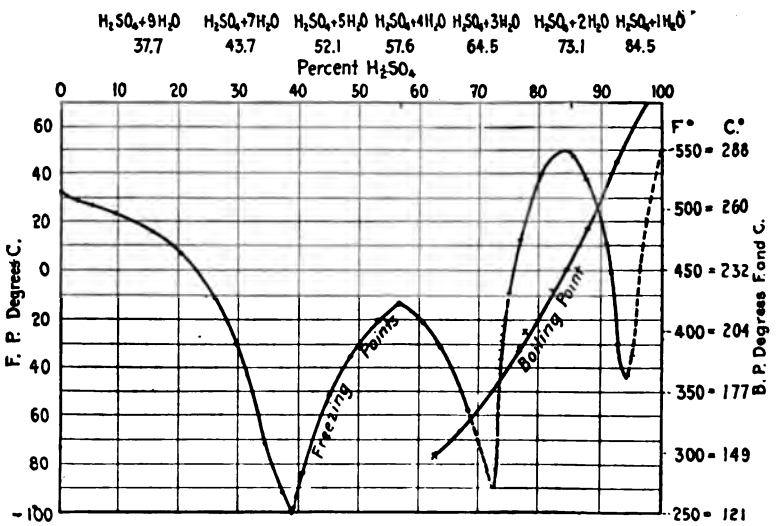

FIG. 78.—Chart Showing Freezing- and Boiling-points of Sulphuric Acid of Varying Concentration.

[1] Ninety-three thousand pounds of sulphuric acid, with an exposed surface of 1260 sq. ft. and depth of 10 in., had decreased in strength from 86 per cent to 52.12 per cent H_2SO_4, after standing in a lead pan, protected from the rain, for 42 days (Sept. 9th to Oct. 21st, 1916). Air was bubbled through a two-liter sample of this acid for seven consecutive days, when the solution was tested and found to contain 52.18 per cent H_2SO_4. The average temperature of the laboratory was 74° F., the average vapor of the air (7 tests) was 0.2223 gram H_2O per standard cubic foot. The average humidity for September and October was 68 per cent; the average temperature 62° F. The average humidity for the past 33 years was 72 per cent; average temperature 57° F.

about 1.4200 (42.7° Bé.). The acid is well mixed and poured into small clean and dry glass-stoppered sample bottles of about 200-cc. capacity. The bottles are carefully sealed and placed aside for use as desired. To determine the exact strength of this standard acid a portion is standardized against the sodium carbonate, prepared according to directions given.

Method of Standardization. Procedure. A catch weight of about 10 grams of the acid is weighed out in a weighing bottle or 100-cc. beaker (10 cc. = approximately 13 grams) and placed aside for titration. The amount of sulphuric acid in the sample (weight of sample multiplied by per cent divided by 100) is neutralized by 1.0808 times its weight of sodium carbonate. As an excess of acid is necessary to drive out all the carbonic acid the following formula is used—(grams H_2SO_4 $-0.05) \times 1.0808$ = weight of Na_2CO_3 required.

The required amount of sodium carbonate is weighed and transferred to a 600-cc. Erlenmeyer flask and 100 cc. of water added. The acid is carefully poured into the flask and the rinsings of the weighing bottle or beaker added. The solution is boiled for 15 minutes to expel CO_2. A small filtering funnel inserted in the neck of the flask prevents loss during the boiling of the acid and carbonate mixture. The excess of acid is titrated with N/5 NaOH, using phenolphthalein indicator, the caustic being added drop by drop until a faint permanent pink color is obtained.

(The sulphuric equivalent to the NaOH added) + (weight of $Na_2CO_3 \times 0.9252$) = weight of pure H_2SO_4 present in the sample.

NOTES. CO_2-free water should be taken in all titrations with phenolphthalein. The indicator contains 1 gram of the compound per liter of 95% alcohol. One cc. of indicator of this strength is required for each titration.

Results should agree to within 0.05%.

The temperature of the acid should be observed at the time of standardization and this noted with results on the bottles containing the standard samples. The coefficient of expansion is .00016+ per degree F. risen in temperature or .000293 per degree C. per cc. of solution.

Normal Sulphuric acid[1] contains 49.043 grams of H_2SO_4 per liter of solution. To make a liter of the normal acid the amount of the standard acid required is calculated by the formula $\frac{100 \times 49.043}{\text{per cent } H_2SO_4 \text{ in standard}} = \text{grams standard acid}$ necessary. The acid is weighed out in a small beaker, a slight excess being taken (0.1 gram). The acid is washed into a liter flask and made to volume. An aliquot portion is standardized against the standard sodium carbonate. The solution may now be adjusted to the exact strength required.

Example.[1] If 25 cc. of the acid is found to contain 1.25 grams H_2SO_4 we find the amount of dilution required as follows: 25 cc. of N/1 H_2SO_4 should contain 1.226075 grams, therefore $1.226075 : 25 :: 1.25 : x$, and $x = \frac{25 \times 1.25}{1.226075}$. Then x minus 25 = the amount of water required for 25 cc. Total dilution = dilution for 25 multiplied by the volume of acid remaining in the flask divided by 25 = cc. water required to make a normal acid solution.

Fifth normal and tenth normal acids[1] may be prepared by diluting the normal acid to five or ten volumes as the case requires.

Gravimetric Methods. Precipitation as $BaSO_4$. Sulphuric acid may be standardized by precipitating as $BaSO_4$ according to the procedure given for sulphur. $BaSO_4 \times 0.4202 = H_2SO_4$.

[1] See formulæ on page 525.

Determination as $(NH_4)_2SO_4$. To 10 cc. of the acid diluted to 50 cc. in a large platinum dish is added NH_4OH until the acid is neutralized and a faint odor of ammonia is perceptible. The solution is evaporated to dryness on the water bath and dried at 100° C. for half an hour. The residue is weighed as $(NH_4)_2SO_4$. $(NH_4)_2SO_4 \times 0.7422 = \text{gram } H_2SO_4$.

Standard Hydrochloric Acid

This acid is occasionally preferred by chemists to sulphuric acid as a standard. At the constant boiling-point, with pressure of 760 mm., hydrochloric acid has a definite composition of 20.242% HCl. For every 10 mm. increase in pressure the percentage drops .024 and for every 10 mm. decrease in pressure the percentage rises .024% HCl. Advantage is taken of this fact in the preparation of standard hydrochloric acid. Strong, pure HCl is distilled, the first 25 or 30 cc. being rejected. The distillate is bottled in 200-cc. glass-stoppered bottles and sealed, a portion being reserved for standardization. The acid is best standardized against sodium carbonate, using the formula, Weight of HCl weighed for analysis minus $0.05) \times 1.4533 = Na_2CO_3$ required. As in case of H_2SO_4 the Na_2CO_3 is weighed out, placed in an Erlenmeyer flask with the acid and boiled to expel CO_2. The excess of HCl is titrated with standard caustic. N/5 NaOH = 0.0072836 gram HCl per cc.

The exact weight of $Na_2CO_3 \times 0.6881 = HCl$. To this add HCl obtained by NaOH titration = total HCl in the sample taken.

The exact amount of HCl being known, normal acid containing 36.468 grams HCl per liter may be made, and by diluting further, fifth normal and tenth normal acids obtained.[1]

Gravimetric Determination of Hydrochloric Acid by Precipitation as AgCl. Hydrochloric acid may be standardized by precipitation with silver nitrate solution by the procedure for determination of chlorine. $AgCl \times 0.2544 = HCl$. It is advisable to heat the sample, diluted to a convenient volume, and add the hot silver nitrate in slight excess of that required by HCl, the amount of the reagent being calculated, e.g., mol. wt. HCl : mol. wt. $AgNO_3$ :: Wt. HCl in sample : x.

Benzoic Acid Standard

Benzoic acid may be obtained in exceedingly pure form by melting the resublimed acid in a covered platinum dish in a constant-temperature oven, at a temperature of 140° C. The acid is poured into test-tubes, cooled, and the sticks bottled for use. The acid does not take up moisture to any appreciable extent, even when exposed to the air for some time, so that it may be weighed without danger of absorption of moisture.

Standard Caustic Solution

Standard normal sodium hydroxide is made by dissolving approximately 50 grams of NaOH sticks with 1 to 2 grams of $Ba(OH)_2$ in 200 to 300 cc. of water and

[1] See formulæ on page 525.

diluting to 1000 cc. The caustic is standardized against normal H_2SO_4, using phenolphthalein indicator. The solution is adjusted to the exact strength desired by addition of distilled water.

NOTE. The addition of $Ba(OH)_2$ is made to precipitate the carbonate in the caustic, as this would interfere with titrations in presence of phenolphthalein. As the presence of barium would produce a cloudiness with H_2SO_4 it is advisable to add only an amount sufficient to precipitate the carbonate.

STANDARD BURETTES

For accurate titration of acids or alkalies it is advisable to have a titration of 75 to 100 cc. Since the straight 100-cc. burette if graduated to twentieths of a cc. would be too long for convenient handling, the chamber burette is used. The chamber located in the upper portion of the apparatus holds 75 cc., the lower portion drawn out into a uniform-bore tube is graduated in twentieths of a cc. Each tenth of a cc. has a mark passing entirely around the tube so that there will be no error in reading, the eye being held so that the mark appears to be a straight line drawn across the tube. The burette is enclosed in a large tube filled with distilled water and carrying a thermometer. The burette is connected, by means of an arm at the base, with a reservoir of standard acid. The cut, Fig. 79, shows the apparatus connected ready for use.

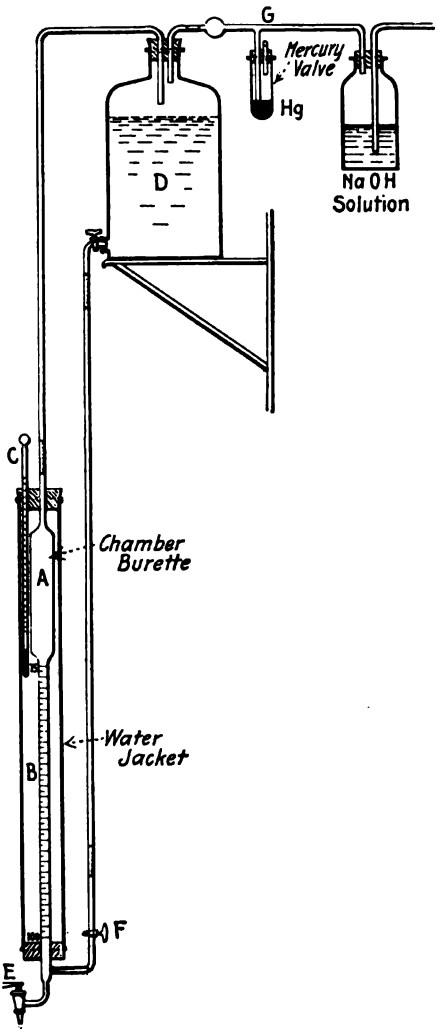

FIG. 79.

If vapor is lost from the standard reagents and this replaced by dry air, as in the common practice, the solution gradually changes in strength. A simple and ingenious device, designed by H. W. Herrig (Gen. Chem. Co.), is shown at the top of Fig. 79, which overcomes this difficulty. The air drawn into the reagent bottle is purified and saturated with moisture by passing it through sodium hydroxide. A mercury valve relieves the pressure if expansion of air in the reagent bottle occurs due to rise of temperature.

METHODS OF WEIGHING ACIDS

Dilute Acids Non-Volatile under Ordinary Conditions

Dilute acids may be weighed directly in a beaker, weighing bottle or ordinary pipette (see directions given later) by measuring out the approximate amount desired. Since a burette reading from 75-cc. to 100-cc. should be used for this work it will be necessary to take such an amount of the acid as will require a titration between these extremes. This may be accomplished by taking the specific gravity of the acid and referring to the table for the approximate strength. From this the volume necessary may readily be calculated.

Example. The case will be taken where a 75-cc. to 100-cc. burette is being used and the titration is to be made with normal caustic solution, the acid titrated is sulphuric acid. The capacity of the burette is $75 \times 0.049 = 3.675$ grams H_2SO_4 to $100 \times 0.049 = 4.9$ grams H_2SO_4. (For HCl the capacity would be 2.74 to 3.65 grams HCl and for HNO_3 it would be 4.73 to 6.3 grams HNO_3).

Suppose the sulphuric acid has a sp.gr. of 1.1600. From the table for H_2SO_4 we find that this acid is 22.25% H_2SO_4, then 1 cc. contains 1.16×22.25 divided by $100 = 0.2581$ gram H_2SO_4. Since the capacity of the burette is 3.675 to 4.9 grams H_2SO_4, we must weigh between $\frac{3.675}{.2225}$ to $\frac{4.9}{.2225}$ grams of the acid; to get this we should take $\frac{3.675}{.2581}$ to $\frac{4.9}{.2581}$ cc., that is to say, 14.5 to 18.5 cc. of the acid, which will weigh 16.8 grams to 21.5 grams.

Weighing Strong Acids, Fuming or Volatile under Ordinary Conditions

The acid must be confined during weighing and until it is mixed with water or standard caustic. The best forms of apparatus include the following:

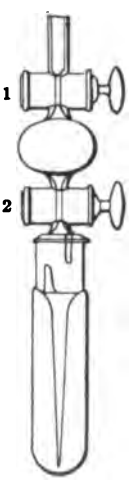

FIG. 80. Lunge-Ray Pipette.

Lunge-Ray Pipette. The pipette is shown in Fig. 80. Two glass stop-cocks confine the acid in a bulb. The lower part of the pipette is protected by a ground-on test-tube. The dry pipette is weighed. Cock 2 is closed and 1 opened and a vacuum produced in the bulb by applying suction at the upper end of pipette and closing stop-cock 1 with suction still on. The sample may now be drawn into the pipette by immersing the lower end in the sample and opening the stop-cock 2, the vacuum producing the suction. The increased weight = acid drawn in. The pipette is emptied by running the acid under water.

Dely Weighing Tube.[1] This form of weighing tube has proven to be of exceptional value, to the busy works-chemist, in the analysis of oleum and mixed acids. Both speed and accuracy are gained by its use. The apparatus, shown in the cut on page 507, consists of a long glass tube of small bore, wound in a spiral coil. Fig. 81.

The sample of acid is drawn into the weighed coil by applying suction through a rubber tube attached to *A* and drawing in the required amount of acid, a mark, ascertained by a previous run being made to indicate the point to which the acid is drawn. The

[1] J. G. Dely, Chemist, Gen. Chem. Co.

tip *B* is carefully wiped off with tissue paper and the tube and sample weighed. The weight of the tube deducted gives the weight of the sample.

The apparatus is now inclined so that the acid runs back into the crook at *C* to a point marked on the wall of the tube, in order to expel as much air as possible from this end. A rubber tube filled with water is attached to *A*, the other end of the rubber tube being connected to a bottle containing distilled water. A glass bead, such as is used in rubber-tipped burettes, fitting snugly in this tube, regulates the flow of water. The Dely tube is now inverted, the tip being immersed in 150 cc. to 200 cc. of distilled water in a 4-in. casserole—Fig. 81. By pressing gently on the bead, water is slowly admitted in the tube, forcing the acid before it. The acid and water are separated by a bubble of air. Before forcing out the last half-inch of acid, the tube connected to the water supply is disconnected and the weak acid from the casserole drawn back into the Dely tube for two or three inches, then again the acid is almost entirely expelled by water from the reservoir and the procedure repeated. This is to absorb the SO_3 gas that invariably is present in the bubble of air above mentioned, which would be lost if forced out directly by the water column. In order to facilitate this last step it is well to have a short rubber tube attached to the Dely tube, and a glass tip in the tube connected with the reservoir of water. The acid in the casserole, upon washing out the Dely tube, is titrated with standard caustic according to the procedure for titration of acids.

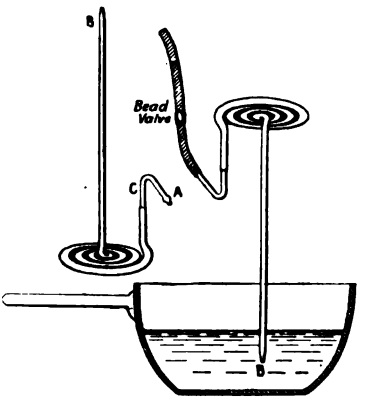

FIG. 81.
Dely Weighing Tube in Operation.

The tube is dried after washing with alcohol, followed by ether, by heating on an asbestos mat on a hot plate, dry air being aspirated through.

Snake Weighing Tube. The snake tube is a simple device that may be easily made by an amateur glass-blower. It is made out of a glass tube 8–10 ins. long, slightly thinner than a lead pencil. One end of the tube is drawn out to capillarity. The tube has a double bend, as shown in the illustration. It is so made that it rests on the double bend with the ends inclined upward to prevent the outflow of the acid. Fig. 82.

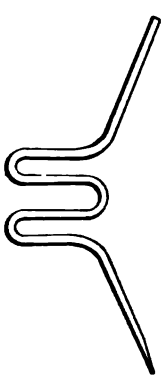

FIG. 82.
Snake Tube.

The tube is dried with alcohol, ether and air treatment, as in case of the Dely tube. After weighing the empty tube, acid is drawn into it by suction through an attached rubber tube. The capillary end that has dipped into the sample is wiped dry with tissue paper. The acid and tube are weighed and the acid estimated by difference.

The acid is run into 150 cc. of water in a casserole, the flow being regulated by the index finger pressed against the larger end of the tube. With careful regulation of the flow, practically no bumping occurs. With a small capillary opening it is not necessary to place the finger over the larger end of the tube as the acid flow will be slow. The tube should be kept in motion to prevent bumping from

overheating any one portion. Kicking back of the acid indicates that the capillary end of the tube is too large. When the contents of the tube have run out, the tube is rinsed by sucking up some acid from the casserole and allowing it to run out, repeating several times. Suction may be applied by means of a rubber bulb attached to the tube. The acid is now titrated with standard caustic, using phenolphthalein indicator.

Blay-Burkhard Graduated Weighing Burette. This apparatus, designed by V. L. Blay and W. E. Burkhard, General Chemical Company, is used for weighing acids or other liquids. The form for general use is shown in Fig. 83. The burette is graduated in half cc. divisions, from 0 to 20 cc. An apparatus half this size is used for oleum, where a 2-cc. sample is sufficient for a determination. For the purpose of running the sample under water a capillary tube (*E*, Fig. 83) with ground joint, is attached to the burette. This tube is placed in the solution during titration. The burette is provided with a glass vented stopper (*A*) on the top, and a glass cap for the tip, both having ground joints, to prevent escape of fumes from the sample.

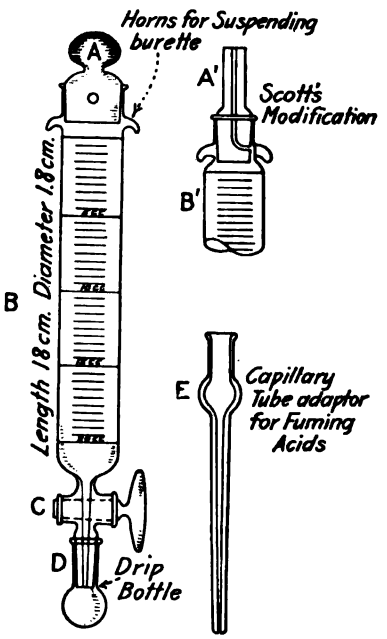

FIG. 83.—Blay-Burkhard Graduated Weighing Burette.

The Editor has modified the apparatus by replacing the fragile cap (*A*) by a tube stopper with capillary vent (see *A'*, Fig. 83). The vent to the air is opened or closed by a slight turn of this stopper. By means of this tube acid may be drawn into the burette according to the Lunge-Ray pipette procedure. With these burettes a man can control his work very accurately and save a great amount of time, both in weighing and manipulation.

In the analysis of strong oleums, Burkhard recommends addition of the acid to a saturated solution of neutral Glauber salt in place of pure water, the reaction being less violent.

The glass-bulb method is still used for analysis of strong oleum. The acid weighed in a sealed tube of known weight is mixed with water by breaking the bulb in a stoppered bottle containing water, the acid is cooled and titrated as usual.

Titration of Acids and Alkalies

In the acid titration the sample is conveniently titrated in a white porcelain casserole. This gives a white background that enables the analyst to see the end-point. The caustic is run into the acid, to within a few cc. of the end-point, rapidly and then cautiously to a faint change of color—faint pink with phenolphthalein or an orange-yellow with methyl-orange. Phenolphthalein is generally preferred to acid titrations. CO_2-free caustic and water should always be used.

ANALYSIS OF MURIATIC ACID

(Commercial Hydrochloric Acid)

Total Acidity and Hydrochloric Acid

The usual titration with standard caustic gives the total acidity, including, in addition to hydrochloric acid, nitric and sulphuric acids which may occur in the commercial product. The acidity due to these acids is deducted from the total acidity to find the actual HCl in the muriatic acid.

A catch weight, 10 to 15 grams of the acid, is weighed in a weighing bottle, or a large snake tube, or the Dely tube, as in case of oleum analysis, and the acid allowed to mix with water in a casserole; methyl-orange indicator is added and the acid titrated with standard normal caustic solution, the red color fading to a lemon-yellow. A fraction of a drop of the alkali will cause the change when the end-point has been reached.

One cc. N/1 NaOH = 0.03647 g. HCl.

NOTE. Hydrochloric acid may be determined gravimetrically by precipitating the chloride with silver nitrate—$HCl + AgNO_3 = AgCl + HNO_3$, or by the volumetric methods for the determination of chlorine. See Chlorine.

Determination of Impurities in Commercial Hydrochloric Acid. Free Chlorine

Five cc. of the acid are diluted to 10 cc., about 5 cc. of fresh starch solution added and a few drops of 5% KI solution together with about 1 cc. of dilute H_2SO_4. A blue color indicates free chlorine. This color may be matched in a Nessler tube with a standard. It is possible to determine .0001% chlorine on a 5-cc. sample.

Nitric Acid or Nitrates in Hydrochloric Acid

About 5 cc. of the hydrochloric acid is cautiously added to 75 cc. of 95% H_2SO_4, the HCl being introduced under the surface of the sulphuric acid. The nitric acid may now be titrated with standard ferrous sulphate by the procedure for the direct determination of nitric acid and nitrates. (Method of Scott and Bowman.) The ferrous sulphate test for nitric is delicate. Traces of nitric acid produce a pink coloration; larger amounts a reddish brown to dark brown. The color is permanent when an excess of ferrous sulphate has been added. See page 515.

Sulphuric Acid and Sulphates in Hydrochloric Acid

Free H_2SO_4. Fifty cc. of the sample is evaporated in a platinum dish (steam bath) to dryness or until the HCl has been expelled. A few drops of water are added and the material again taken to dryness (steam bath). The residue is taken up with water and titrated with N/10 NaOH, using methyl-orange indicator. One cc. = 0.0049043 gram H_2SO_4.

Total Sulphates. Fifty cc. of the muriatic acid is evaporated to about 5 to 10 cc. and then diluted to about 200 cc. and heated to boiling. Total SO_3 is now precipitated by adding $BaCl_2$ solution as in case of determination of total sulphur. The precipitated $BaSO_4$ includes the free H_2SO_4 and the combined SO_3. $BaSO_4 \times 0.4202 = H_2SO_4$.

Arsenic in Hydrochloric Acid

Commercial muriatic acid may contain arsenic. This is best determined by the Gutzeit Method given in detail under Arsenic. 10 cc. of sample is usually sufficient for this determination. If much arsenic is present the distillation method may be followed, using a 25 to 50-cc. sample. The distillate is titrated with standard iodine according to procedure given for arsenic by the iodine titration, page 39.

Barium Chloride in Hydrochloric Acid

Fifty cc. is evaporated to dryness and then over a low flame to expel SO_2. The residue is taken up with 1 cc. of 1 : 1 HCl and 50 cc. of water. 1 cc. H_2SO_4 is added and the precipitated $BaSO_4$ filtered off and weighed. If silica is present in the sample its weight should be deducted. $BaSO_4 \times 0.8923 = BaCl_2$.

Total Solids and Silica

One hundred cc. of the HCl in a platinum dish is evaporated to dryness and the residue ignited and weighed. 5 cc. of HF is added with a few drops of H_2SO_4 and the solution again evaporated and ignited. *The first weight = total solids. The loss of weight in the second ignition = SiO_2.*

ANALYSIS OF HYDROFLUORIC ACID

The following constituents—hydrofluosilicic sulphuric and sulphurous acids—commonly occurring with hydrofluoric acid, are determined in the analysis, along with the hydrofluoric acid, by titration. Generally the acid contains a slight residue upon ignition. The titrations are made in presence of KNO_3, first ice cold, and then completed at 80° C. or more. The cold titration gives the hydrofluoric, sulphuric and sulphurous acids and one-third of the hydrofluosilicic acid and upon heating the titration gives the remaining two-thirds of the H_2SiF_6, the following reactions taking place. Titration cold, $H_2SiF_6 + 2KNO_3 = K_2SiF_6 + 2HNO_3 (= \frac{1}{3} H_2SiF_6)$. The liberated $2HNO_3$ requiring 2NaOH. Titration hot. $K_2SiF_6 + 4NaOH = 4NaF + 2KF + SiO_2 + 2H_2O (\frac{2}{3} H_2SiF_6)$.

The sulphuric acid is determined by titration with NaOH, upon expulsion of the accompanying more volatile acids. Sulphurous acid is determined by titration with standard iodine.

Special Apparatus. Chamber burette graduated from 75 to 100 cc. in $\frac{1}{20}$ cc. as described under the determination of sulphuric acid, oleum, mixed acids, etc.

Platinum weighing tube. Length about 5 cm., diameter 1.4 cm. The tube fitted with a platinum cap with a loop top to facilitate removal by means of a platinum wire.

Lead thief for sampling.

Special Reagents.

Normal solution of NaOH. 1 cc. = .04903 gram H_2SO_4.

N/10 Iodine solution. 1 cc. = .0041 gram H_2SO_3.

Phenolphthalein indicator, and Starch solution.

Details of Procedure. Total Acidity and Hydrofluosilicic Acid

A catch weight of the acid is taken by pouring the acid by means of the thief or directly from the paraffine bottle into the platinum weighing bottle, such a weight being taken as will require a titration of from 75 to 100 cc. of the normal caustic solution. (This may be judged by a preliminary run if the approximate value is not known.)

About 10 cc. of a saturated solution of KNO_3 is poured into a large platinum dish (capacity about 125 cc.), and chipped ice added. About 50 cc. of N/1 NaOH solution is run in from a burette and three drops of the strong phenolphthalein added. The platinum weighing bottle containing the sample is inverted beneath the surface of the caustic, the cover cautiously removed from the bottle by means of a heavy platinum wire, so as to allow the acid to mix very gradually with the standard NaOH (rapid addition is apt to cause loss of acid by fumes). Standard N/1 NaOH is added from the burette until the first permanent pink color is obtained. (The end-point will be uncertain and fading unless the solution is kept cold—0° C.) The reading of the burette is noted—total $\frac{\text{N/1 NaOH}}{\text{Wt. of sample}} = \text{A}$. The dish is now placed on a hot plate and the solution warmed to about 80° C. and the titration completed with the N/1 NaOH solution to a permanent pink. Additional cc. required divided by weight of sample = B. (See calculation at close of procedure.)

Sulphuric Acid in Hydrofluoric Acid

About 5 grams of the sample are weighed in the platinum capsule and transferred to a large platinum dish, the capsule being rinsed out into the dish with water. The solution is evaporated on the steam bath to small volume (the evaporation is assisted by passing a hot current of pure dry air over the sample, see procedure for oleum), a few drops of water are added and the evaporation repeated; no odor should be perceptible, all the hydrofluoric, hydrofluosilicic and sulphurous acids being expelled. The sulphuric acid is cooled, taken up with 100 cc. of CO_2-free water, three drops of strong phenolphthalein added and the acid titrated with N/1 NaOH solution in a 50-cc. burette. The cc. titration divided by the weight of the sample is noted as C. (See calculations at the close of the procedure.)

Sulphurous Acid in Hydrofluoric Acid

Ten grams of the sample are weighed in a tared platinum capsule with cover and washed into a large platinum dish with about 75 cc. of water. N/10 Iodine solution is added to a faint yellow. The end point is made more distinct by addition of a little starch solution near the end of the reaction.

One cc. of N/10 I = 0.0041 g. H_2SO_3. cc. N/10 I ÷ wt. of sample = D.

Calculation of Results.

Factors. $H_2SO_4 \times 0.4904 = H_2SiF_6$.

$H_2SO_4 \times 0.4080 = HF$.

One cc. N/10 I = 0.0041 g. H_2SO_3.

Symbols. $A = \frac{\text{cc. NaOH for total acidity (cold)}}{\text{Weight of sample}}$.

$B = \frac{\text{cc. of NaOH additional for } H_2SiF_6 \text{ (hot)}}{\text{Weight of sample}}$.

$C = \frac{\text{cc. NaOH for } H_2SO_4}{\text{Weight of sample}}$.

$D = \frac{\text{cc. N/10 iodine.}}{\text{Weight of sample}}$.

Formulæ for Calculation. If E = value of 1 cc. of the standard N/1 caustic in terms of H_2SO_4 then

$$\text{Per cent HF} = \left(A - \frac{B}{2} - C\right) \times E \times 0.408 \times 100 - 0.2D:$$

$$\text{Per cent } H_2SiF_6 = \frac{3}{2} B \times E \times 0.4904 \times 100;$$

$$\text{Per cent } H_2SO_4 = C \times E \times 100;$$

$$\text{Per cent } H_2SO_3 = D \times 0.0041 \times 100.$$

Residue. This is determined by evaporation of 15 to 20 grams of the acid in a platinum dish, and gentle ignition of the dry residue.

NOTES AND PRECAUTIONS. Weighings should be made quickly in covered platinum weighing bottles.

The end-point in the cold titration is the first pink that persists for 15 seconds.

It is advisable to weigh out the sample for the sulphuric acid determination first and start the evaporation to facilitate more rapid results.

Iodine is preferred to permanganate for titration of H_2SO_3 as the latter also titrates organic matter that is apt to occur in the acid.

The residue contains Fe_2O_3, Al_2O_3, $CaSO_4$, CaF, Alkalies, etc.

COMPLETE ANALYSIS OF NITRIC ACID

The acidity of nitric acid obtained by titration with standard caustic may be due not only to HNO_3 but to impurities H_2SO_4, HCl and lower oxides of nitrogen, hence for extremely accurate analysis it is essential to look for these impurities and make allowances accordingly if they are found to be present. Nitric acid may be determined directly by titration with ferrous sulphate according to the procedure given in detail, page 515; this titration will include combined nitrates as well as the free acid, whereas the titration with caustic includes only free acids. In addition to the above-mentioned impurities, commercial nitric acid frequently contains free chlorine, chlorides, chlorates, iodine, iodides, iodates, silica, and suspended solids; the last is reported as insoluble residue. In an analysis of nitric acid the impurities, which are known to be injurious to the art for which the acid is used, are looked for and determined if present.

Determination of Total Acidity

As in case of mixed acids and, in fact, all accurate determinations of acids with caustic, such an amount of the sample should be taken as will require a titration within the limits of the standard chamber burette—75 to 100 cc. For normal caustic this would require 4.726 to 6.3 grams of 100% HNO_3 or a fifth or tenth of thi amount for N/5 or N/10 NaOH. From the specific gravity of the acid its approximate strength can be obtained by referring to the table for nitric acid and calculating the volume and approximate weight required for analysis (see example under Methods of Weighing Acids—Dilute Acids—Non-Volatile under Ordinary Conditions, page 506).

The acid is weighed in a weighing bottle, or in the Dely weighing tube or Lunge-Ray pipette if it is a fuming acid. The titration is made in a casserole, the acid being mixed with 150 to 200 cc. of CO_2 free water and titrated in presence of phenolphthalein indicator. (Methyl-orange is destroyed by nitrous acid.) The total acidity is expressed in terms of H_2SO_4 if other acids are present.

$$\frac{\text{cc. N/1 NaOH} \times .049043 \times 100}{\text{Weight of the sample}} = \text{per cent } H_2SO_4 \text{ equivalent.}$$

$H_2SO_4 \times 1.285 = HNO_3$.

Direct calculation to HNO_3 $\dfrac{\text{cc. N/1 NaOH} \times 0.063018 \times 100}{\text{Weight of the sample}} = \text{per cent } HNO_3$.

Determination of Sulphuric Acid in Nitric Acid

About 10 grams of the acid are evaporated to dryness on the steam bath. The residue is taken up with about 10 cc. of water and the evaporation repeated until free from nitric fumes, the residue finally diluted to 100 cc. and the sulphuric acid titrated with N/5 NaOH, using phenolphthalein or methyl-orange indicator. Gravimetrically the acid may be precipitated from a hot solution as $BaSO_4$ by addition of barium chloride reagent according to the method for determining sulphur.

One cc. N/5 NaOH = 0.009809 gram H_2SO_4.

$BaSO_4 \times 0.4202 = H_2SO_4$. Per cent = 100 divided by weight of sample $\times H_2SO_4$ obtained.

Determination of Hydrochloric Acid in Nitric Acid

A 5- to 50-gram sample is taken, that is to say, a sufficient amount of the acid so that a weighable amount of AgCl may be obtained. The sample is nearly neutralized with NH_4OH (it should be slightly acid with HNO_3) and a slight excess of silver nitrate reagent added to the hot solution; the mixture is stirred thoroughly, then allowed to settle for one or two hours. The AgCl is filtered through a weighed Gooch crucible containing an asbestos mat, then washed, dried and ignited at a low red heat. (See general method for the determination of chlorine.)

Factors. $AgCl \times 0.2474 = Cl$. $AgCl \times 0.2544 = HCl$.

$AgCl \times 0.34212 =$ equivalent H_2SO_4.

Find the per cent HCl and the per cent equivalent H_2SO_4.

Lower Oxides. Determined as Nitrous Acid

For practical purposes the lower oxides of nitrogen that may be present in nitric acid are calculated to N_2O_3 or HNO_2. If it is desired to report these as N_2O_4 the conversion factor given below may be used. The lower oxides may be obtained by titration with standard permanganate, other reducing agents being absent. In presence of organic matter titration with standard iodine solution should be made. (See general procedure for determination of nitrous acid, etc.)

It makes but little difference whether the permanganate is added to the sample containing nitrite or the sample added to a measured amount of permanganate, provided in the first method the titration be made as rapidly as possible to prevent oxidation taking place due to dilution of the sample with water. The end-point in the first procedure is quicker and sharper.

Potassium permanganate oxidizes nitrous acid to nitric according to the reaction $2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O$. Therefore 1 cc. of N/1 $KMnO_4=0.02351$ gram HNO_2 or 0.019 gram N_2O_3.

Twenty-five cc. of the acid are diluted in a casserole to about 300 cc. with cold water, and 25 cc. of dilute H_2SO_4, 1 : 4 added. The solution is titrated immediately with N/5 $KMnO_4$, the reagent being added rapidly at first and finally drop by drop as the end-point is approached. The reaction near the end is apt to be slow, so that time must be allowed for complete oxidation. The titration is completed when a pink color is obtained, that persists for three minutes.

$$\text{cc. N/5 } KMnO_4 \times 0.004702 = \text{gram } HNO_2.$$

The result multiplied by $\frac{100}{\text{wt. sample}} = \text{per cent.}$

$$HNO_2 \times 1.0431 = \text{equivalent } H_2SO_4.$$

Nitric Acid

From the total acidity expressed as H_2SO_4 is subtracted the acidity due to HCl and HNO_2 (lower oxides of nitrogen) expressed in terms of H_2SO_4. The remainder is due to nitric acid, in terms of sulphuric acid.

$$H_2SO_4 \times 1.285 = HNO_3.$$

Determination of Iodine in Nitric Acid

Fifty cc. of the acid in an Erlenmeyer flask is neutralized with caustic, the mixture being cooled in running water during the operation. The solution, poured into a separatory funnel, is made acid with dilute H_2SO_4 and a few drops of 1% solution of KNO_2 added, followed by about 25 cc. of CS_2 or CCl_4. The mixture is shaken to extract the free iodine and the CS_2 or CCl_4 drawn off and the extraction repeated by addition of KNO_2 and CS_2 or CCl_4 until all the iodine has been extracted. Iodine present as iodide is extracted by this method. To obtain the iodine from iodate, H_2S water is added and the extraction with addition of $NaNO_2$ and CS_2 repeated.

The combined extracts are washed in a separatory funnel until free of acid. The iodine is now titrated with standard sodium thiosulphate by adding 25 to

30 cc. of water together with 5 cc. of 1% sodium bicarbonate solution (10 grams $NaHCO_3$ per liter+1 cc. HCl).

One cc. N/10 $Na_2S_2O_3$ = 0.01269 gram I.

Reactions.

$$2HI+2KNO_2+H_2SO_4=K_2SO_4+2H_2O+I_2+2NO;$$

$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6.$$

Determination of Free Chlorine in Nitric Acid

When a current of pure air is passed into nitric acid containing free chlorine the air blows out the chlorine. If air aspirated through a sample of nitric acid is passed through a solution of potassium iodide the free chlorine will displace the iodine. The liberated iodine may now be titrated with standard sodium thiosulphate and the equivalent chlorine calculated.

Total Non-Volatile Solids

These may be determined by evaporating a large sample of 100 to 200 cc. of the nitric acid to dryness. The residue is heated gently to expel the last traces of nitric acid and then washed into a platinum dish, again evaporated to dryness and ignited to a dull red heat. The residue is due to non-volatile solids.

FERROUS SULPHATE METHOD FOR THE DIRECT DETERMINATION OF NITRIC ACID[1]

Although the test for nitric acid by ferrous sulphate in presence of strong sulphuric acid has long been known, the reagent has not been used for an accurate quantitative method until F. C. Bowman and W. W. Scott, General Chemical Company, developed the procedure herein given. Nitric acid may be determined quantitatively in arsenic acid by titration with ferrous sulphate containing free sulphuric acid. The method is also applicable to the determination of nitric acid in phosphoric acid and in sulphuric acid, including oleums and mixed acids. The reaction in phosphoric acid and arsenic acid goes further than it does in sulphuric acid. The following equations represent the reactions taking place:

Reaction in Arsenic or Phosphoric Acids:

$$6FeSO_4+2HNO_3+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O.$$

Reaction in Sulphuric Acid:

$$4FeSO_4+2HNO_3+2H_2SO_4=2Fe_2(SO_4)_3+N_2O_2+3H_2O.$$

Oxidizing agents such as chlorates, iodates, bromates, etc., interfere, owing to their oxidizing action on ferrous sulphate, hence these should be absent from the sample or allowance made, if appreciable amounts are present. NaCl up to .002 gram does not interfere; larger amounts tend to lower results. KI and KBr react in a similar manner to NaCl, 0.002 gram causing no interference. KNO_3

[1] The Jour. Ind. Eng. Chem., 7, 766, 1915.

present in amounts up to 50% of the HNO_3 does not interfere. The sample should not contain over 25% water, nor should the temperature exceed 60° C. during titration. 0.1 to 0.8 gram HNO_3 are accurately titrated, in sulphuric acid.

Special Reagents Required. ***Standard Ferrous Sulphate.***

A. Reagent to be Used in Titration of Nitric Acid in Sulphuric Acid, Oleum, etc. 176.5 grams of $FeSO_4 \cdot 7H_2O$ are dissolved in about 400 cc. of water, and 500 cc. of about 60% H_2SO_4 (1 vol. 66° Bé. acid per 1 vol. H_2O) are added with constant stirring, and the solution (cooled if necessary) made up to 1000 cc. 1 cc. will be equivalent to 0.02± gram HNO_3, the exact value being determined by standardization.

B. Reagent for Titration of Nitric in Phosphoric or Arsenic Acid. Ferrous sulphate to be used, should be made up as follows: 264.7 grams of $FeSO_4 \cdot 7H_2O$ is dissolved in 500 cc. of water, 50 cc. of 66° Bé. H_2SO_4 (93.2%), added and the solution made up to 1000 cc. 1 cc. will be equal to approximately 0.02 gram HNO_3. The exact strength is ascertained by titrating a known amount of nitric acid in phosphoric or arsenic acid upon warming to 40° or 50° C.

Standard Nitric Acid. The acid should contain about 40 grams of HNO_3 (100%) per liter of solution, e.g., 41 cc. of the desk reagent (sp.gr. 1.42) per liter will give the strength desired, the exact value being determined by titration of the acid against standard caustic.

Potassium Dichromate, N/2 $K_2Cr_2O_7$ Solution. The exact value in terms of iron should be known.

Standardization of Ferrous Sulphate Reagent

1. Titration against standard nitric acid.

A. Reagent to be Used for Determination of Nitric in Sulphuric Acid. 10 cc. of the standard $HNO_3 = 0.4\pm$ g. (the exact amount having been ascertained), is run into 100 cc. of 66° Bé. (93.2%) H_2SO_4, free from oxidizing agents (HNO_3, etc.) and the resulting mixture titrated with the standard $FeSO_4$ solution according to the directions given under the General Procedure for determining HNO_3 in H_2SO_4, page 517.

Weight of HNO_3 taken divided by cc. of $FeSO_4$ minus 0.2 cc. [1] = grams HNO_3 cc. $FeSO_4$.

B. Standardization of the Reagent Used in the Determination of Nitric in Arsenic and Phosphoric Acids. 10 cc. of the standard $HNO_3 = 0.4\pm$ gram (the exact amount having been ascertained) is run into 100 cc. of H_2AsO_4, or H_3PO_4 according to the product to be titrated, the mixture warmed and titrated according to directions given under Procedure for determination of HNO_3 in arsenic or phosphoric acid.

Weight of HNO_3 taken, divided by cc. $FeSO_4$ = grams HNO_3 per cc. $FeSO_4$

2. Standardizing Ferrous Sulphate with Standard Potassium Dichromate.

A. Reagent to be Used in Determination of Nitric in Sulphuric Acid. 25 cc. of N/2 $K_2Cr_2O_7$ (or 125 cc. N/10 $K_2Cr_2O_7$), are accurately measured out

[1] An excess of 0.2 cc. $FeSO_4$ is required to produce the desired color reaction in 100 cc. of pure H_2SO_4. A larger blank is frequently required, as HNO_3 occurs as an impurity in H_2SO_4. 100 cc. should be tested for HNO_3 and, if present, the blank substituted for the constant 0.2 cc. The burette should be allowed to drain three minutes before taking the reading.

into a 250-cc. beaker and the solution titrated with the $FeSO_4$ reagent, until the first fraction of a drop of excess produces a blue color with potassium ferricyanide indicator on a spot plate. Usually between 19 to 20 cc. are required. The iron value of the dichromate multiplied by 0.6543 = gram HNO_3 for the total cc. of $FeSO_4$ required in the titration.

Calculation.

Since N/2 $K_2Cr_2O_7$ = 0.024517 gram salt, 1 gram $K_2Cr_2O_7$ = 1.13882 Fe, therefore 25 cc. = 0.024517 × 1.13882 × 0.5643 × 25 = 0.3939 gram HNO_3 equivalent.

0.3939 divided by cc. $FeSO_4$ required in the titration = grams HNO_3 equivalent per cc.

B. Reagent to be Used in Determination of HNO_3 in H_3AsO_4 or H_3PO_4. 38 cc. of $K_2Cr_2O_7$ solution are titrated with $FeSO_4$ according to directions given in "A". The Fe value multiplied by 0.3762 = gram HNO_3.

Calculation. 38 cc. of $K_2Cr_2O_7$ = 0.024517 × 1.13882 × 0.3762 × 38 = 0.3991 gram HNO_3 equivalent. 0.3991 divided by cc. $FeSO_4$ required in the titration = grams HNO_3 equivalent per c.c.

Factors.

$K_2Cr_2O_7$ to Fe = 1.13882, reciprocal = 0.8781.

2Fe to HNO_3 = 0.5643, recip. = 1.7722. 3Fe to HNO_3 = 0.3762, recip. = 2.6582.

HNO_3 to $2FeSO_4.7H_2O$ = 8.8235 recip. = 0.1133.

HNO_3 to $3FeSO_4.7H_2O$ = 13.2348, recip. = 0.07556.

$K_2Cr_2O_7$ to HNO_3 = 0.6426, recip. = 1.5562. (Titration of A reagent.)

$K_2Cr_2O_7$ to HNO_3 = 0.4284, recip. = 2.3342. (Titration of B reagent.)

NOTE. The two procedures for standardization agree closely. The following results were obtained on a check standardization by the two procedures:

HNO_3 as Standard − HNO_3 equivalent = 0.02068, average of 4 closely agreeing titrations.

$K_2Cr_2O_7$ as Standard − HNO_3 equivalent = 0.02073, average of 4 closely agreeing titrations.

Runs by two men working independently checked within 0.1 cc.

General Procedure. Determination of Nitric Acid in Sulphuric Acid

The procedure is applicable to the determination of nitric acid, free or combined as nitrate, sulphuric acid being used as the medium in which the titration is made. Although 0.1 to 0.8 gram HNO_3 may be accurately titrated, it is a general practice to have the nitric acid content of the sample taken for the titration about the same as the amount taken in standardization of the $FeSO_4$ reagent. A preliminary run on the original material is made, if the approximate nitric acid content is not known. Solids are dissolved in water and made to the desired volume, strong HNO_3 is diluted with water, in either case the dilution should be such that 10 cc. of the solution will contain approximately 0.4 gram HNO_3. Mixed acids and oleum containing over 10% HNO_3 should be mixed with additional 66° Bé. (93+per cent H_2SO_4) and made to a definite volume, an aliquot part being taken for titration.

Evaluation of Nitric Acid

If the nitric acid is known to be free of other
with caustic; combined nitrate cannot be titrated
rately determined by the ferrous sulphate metho
of the HNO_3 or salt having been determined on 1
terial is a solid), the requisite amount is weighe
of which should contain not more than 0.8 gram o
erably about 0.4 gram.

Example. Suppose 1 cc. required a titration
require a titration of 438 cc., whereas 20 cc. is desire
imately 22, e.g., the dilution should be to 22 volume
to 500 cc. will give a mixture of the desired str
weighed in a weighing bottle, the acid washed into
the graduated 500-cc. flask and made to volume.
made in two or three minutes.

Titration. A 250-cc. beaker containing 100 cc
(93+%) is placed in a large casserole or deep porcela
10 cc. of the sample are measured out in an accurate
to contain exactly 10 cc. The solution is run under
acid, the delivery tip of the pipette being kept in con
vent too much local heating. Since the sides of the
the pipette should be kept against the sides in the c
livery. By this procedure loss of nitric acid is reduce

The ferrous sulphate solution is now added from a
the yellow color that first forms takes on a faint b
The pipette is now rinsed out by sucking up the mixtu
the beaker. The titration is now completed, adding th
drop until the yellowish brown color again appears
an appreciable darkening of the solution. A larger
red color. With small amounts of HNO_3 a pink color
the yellowish brown. The end-point once recognized is

Calculation. The cc. titration minus the constant l

the factor for $FeSO_4$ = weight of HNO_3 in the sample

per cent HNO_3.

Example. Suppose 10 cc. equivalent to 1/50 of a 42-

22 cc. $FeSO_4$ whose value = 0.02 g. HNO_3 per cc., then

Determination of Nitric Acid in Oleum or Ferrous Sulphate Method

The rapidity and accuracy of the method for determin
acid makes it valuable for determining nitric acid in ol
Nitrated oleums may be weighed and titrated without

[1] The author (W. W. Scott) found this method exceed
synthetic nitric acid made by himself, during his investig
this acid from its elements.

[2] See Correction Factor, page 519.

...ining large percentages of nitric acid, however, require dilution ...ated under General Procedure.

...The sample may be weighed in a Dely weighing tube (see analysis of ... acids), or in a standard pipette (5 cc. generally taken = 9.61 grams). ...ed, the sample is sucked into the pipette, a rubber tube, with glass ...g attached to the upper end, to which suction is applied without ...ng SO_3 fumes into the mouth. A little vaseline placed on the tip ... prevents loss of acid during the weighing. In routine analysis, ... number of daily samples of oleum are analyzed, and the specific ... oleum does not vary appreciably, 5- to 10-cc. samples may be drawn ... of a pipette, and titrated without weighing, the weight being cal- ... the gravity.

... is run under cold concentrated H_2SO_4 (93%), and titrated according ... under General Procedure for Nitric acid. A blank of 0.2 cc.[1] having ...ed, cc. $FeSO_4 \times HNO_3$ factor for $FeSO_4 \times 100$ divided by wt. taken ... HNO_3.

...n Factor. In making a number of runs with varying amounts of HNO_3, ...d that small quantities of nitric acid required a proportional greater amount ...an larger quantities of HNO_3. For example, 0.07392 gram HNO_3 required ...O_4, four times the amount of HNO_3 required 15 cc. $FeSO_4$, in place of 15.6, ...d six times 0.07392 gram HNO_3 required 22.5 cc. $FeSO_4$ in place of 23.4. It ...ved that even traces of HNO_3 required a titration of over 0.2 cc. It is evi- ... a deduction of 0.2 cc. makes the titrations multiples of the lowest, e.g., 3.7, ...22.3. Again it was found that standardization of $FeSO_4$ with HNO_3 checked ...omate factor when 0.2 cc. was deducted from the first series of titrations. This ...e conclusion that a constant blank of 0.2 cc. should be deducted from the ferrous ... titrations of nitric acid in presence of 100 cc. of nitric free sulphuric acid, ...).

...parison of results:

...O_4 value by HNO_3 corrected = 0.02067 gram. Uncorrected = 0.02045 gram HNO_3.

...O_4 value by $K_2Cr_2O_7$ titration = 0.02083 gram HNO_3.

...curacy of the Ferrous Sulphate Method. Results obtained by the ferrous sul- ... method agree closely with those obtained by the nitrometer. The following ... were obtained by Mr. B. S. Clark,[2] by the $FeSO_4$ method, on nitrated oleums. ...figures below the first row are checks obtained on these samples by purchasers of ...cid, the nitrometer method being used.

...O_4 method.	2.40; 2.82; 3.23; 3.35; 3.52; 3.50; 3.48; 3.57; 3.53; 3.56.
...rometer method.	2.35; 2.79; 3.26; 3.39; 3.57; 3.53; 3.50; 3.58; 3.57; 3.56.
...ference.	0.05; 0.03; 0.03; 0.04; 0.05; 0.03; 0.02; 0.01; 0.04; 0.00.

...termination of Nitric Acid in Arsenic and Phosphoric Acids by the Ferrous Sulphate Method

A direct procedure for the determination of nitric acid in arsenic acid or phos- ...ric acid has been sought on account of the inaccuracy of the evaporation ...hod, since it is difficult to completely expel HNO_3 from these acids. Ferrous

[1] Back titrations of the excess of $FeSO_4$ may be made with standard $K_2Cr_2O_7$, using ferricyanide spot test for ferrous iron.
Sp.gr. of twelve average samples of oleum had a difference of only 0.01. 5 cc. ...ghs 9.61 grams. This is found convenient for analysis. 10 cc. = 19.22 grams will ...ally give a titration of about 20+cc. on the usual nitrated oleum.
[2] Formerly Chemist U. S. Works, G.C.C., Camden, N. J.

sulphate, in presence of sulphuric acid, quantitatively titrates nitric in arsenic acid, the following reaction taking place:

$$6FeSO_4+2HNO_3+3H_2SO_4+xH_3AsO_4=3Fe_2(SO_4)_3+2NO+4H_2O+xH_3AsO_4.$$

The procedure is applicable to the determination of nitric acid in phosphoric acid, the end-point being sharper in this acid than in arsenic. The procedure gives very excellent results in either acid and is recommended for accuracy and rapidity.

Standardization of Ferrous Sulphate has already been given under special reagents. It must be remembered that the arsenic or phosphoric acid diluents should be free from nitric acid or the blank on 100 cc. be ascertained and deducted from titrations made in this diluent.

Procedure. The amount of the sample to be taken is governed by the nitric acid present as an impurity. This may be quickly determined by a preliminary run on a 10-cc. sample, the diluent being the same acid (HNO_3 free) as the acid titrated.

Example. Suppose 10 cc. require a titration of 4.5 cc. of $FeSO_4$, whereas a titration of 20 cc. is desired, then $20\times10\div4.5=44.44$ cc. of the sample required.

The required amount of the acid is measured out and weighed, if its sp.gr. is not known. The acid is poured into a 4-in. casserole and diluted with 100 cc. of nitric free acid of the same kind as that being titrated. The mixture is gently warmed to 40 to 50° C. and titrated with standard ferrous sulphate reagent to a permanent yellowish brown. Towards the end of the titration the acid will boil with each addition of the $FeSO_4$ and the characteristic reddish yellow fumes will be given off. (This does not occur in titrations of HNO_3 in H_2SO_4.)

When very small amounts of nitric acid are present it is often necessary to add a known amount of HNO_3 to start the reaction. The titration in excess of that required by the added HNO_3 is due to the nitric acid in the sample. Very small amounts of HNO_3 produce a pink color.

Calculation cc. $FeSO_4\times HNO_3$ factor for $FeSO_4\times100$ divided by weight taken = per cent HNO_3.

Factors. Fe to $HNO_3=0.3762$. Reciprocal $=2.6582$.

NOTE. In a 20-gram sample 1 cc. 0.02 reagent = 0.1% per cc.

DETERMINATION OF NITROUS ACID OR NITRITE PERMANGANATE METHOD

Principle. Potassium permanganate reacts with nitrous acid or a nitrite as follows:

$$5N_2O_3+4KMnO_4+6H_2SO_4=5N_2O_5+2K_2SO_4+4MnSO_4+6H_2O.$$

$$5HNO_2+2KMnO_4+3H_2SO_4=5HNO_3+K_2SO_4+2MnSO_4+3H_2O.$$

Since $2KMnO_4$ in acid solution has five available oxygens for oxidation of substances (e.g., $2KMnO_4=K_2O.2MnO+5O$ equivalent to 10H) the molecular weights of the constituents divided by 20 in the first equation and by 10 in the second would represent the normal weights per liter, e.g., $5N_2O_3$ divided by 20 = 76 divided by

4 = 19 grams N_2O_3 per liter. $4KMnO_4$ divided by 20 or $2KMnO_4$ divided by 10 = 158.03 divided by 5 = 31.61 grams of $KMnO_4$ per liter for a normal solution. In the second equation if Na represents the univalent element we would have $5NaNO_2$ divided by 10 or 69 divided by 2 = 34.5 grams per liter. Hence 1 cc. of a normal $KMnO_4$ solution would oxidize 0.019 gram N_2O_3 or 0.0345 gram $NaNO_2$ to form N_2O_5 and $NaNO_3$ respectively.

Organic matter is also oxidized by $KMnO_4$ hence will interfere if present.

Special Reagents.

N/5 Potassium Permanganate. The solution contains 6.322 grams $KMnO_4$ per liter.

N/5 Sodium Oxalate. $Na_2C_2O_4$ reacts with $KMnO_4$ as follows:

$$5Na_2C_2O_4+2KMnO_4+8H_2SO_4=K_2SO_4+2MnSO_4+5Na_2SO_4+10CO_2+8H_2O.$$

Hence $5Na_2C_2O_4$ divided by 10 or 134 divided by 2 = 67 grams per liter = a normal sodium oxalate solution. A N/5 solution requires 13.4 grams $Na_2C_2O_4$ per liter.

Preparation of the Sample.

Soluble Nitrites. Ten grams of the nitrite are dissolved in water and made to 1000 cc.; 10 cc. contain 0.1 gram of the sample.

Water-insoluble Nitrites. 0.5 to 1.0 gram of the nitrite according to the amount of nitrous acid present is taken for analysis. An excess of $KMnO_4$ solution is added, followed by dilute H_2SO_4 and the excess standard permanganate titrated with sodium oxalate according to directions given under Procedure.

Nitrous Acid in Nitric Acid and Mixed Acids. This is present generally in very small amounts so that a large sample is taken. The amount and details of the procedures are given under the special subject.

Procedure. For accurate work a chamber burette is recommended, as in case of titration of acids, graduated from 50 cc. to 100 cc. Since the readings will fall between these extremes the sample should contain an equivalent of 0.19 to 0.38 gram N_2O_3, or 0.345 to 0.69 gram $NaNO_2$ or 0.426 to 0.85 gram KNO_2. In soluble commercial nitrites, $NaNO_2$ or KNO_2, 50 cc. of the above solution (0.5 gram) are generally sufficient for titration. A preliminary run will show approximately the amount of nitrite present and the amount of sample taken is governed accordingly.

For routine work where a number of daily determinations are made, a 50-cc. burette is generally preferred. Half the above samples must then be taken.

Trial Run. If the approximate strength of the salt is not known the following test may be quickly made to ascertain whether more than 50 cc. of solution is necessary and the approximate amount of $KMnO_4$ required for oxidation.

Ten cc. of the solution together with 100 cc. of water are placed in a 4-in. casserole and about 10 cc. of dilute H_2SO_4, 1 : 1, added. Standard $KMnO_4$ from a 50-cc. burette is now run into the sample until a permanent pink color is obtained. The cc. of $KMnO_4$ multiplied by 5 = the approximate amount of permanganate solution required for oxidation of 50 cc. of sample. An excess of 5 to 10 cc. should be taken in the regular run.

Titration of Nitrite. Fifty cc. of the solution (or more or less as the case may require) are placed in a 4-in. casserole and standard $KMnO_4$ added in quantity sufficient to completely oxidize the nitrite together with 5 to 10 cc. in excess, as ascertained by the trial run. Ten cc. of dilute H_2SO_4 are added and the sample

placed on the hot plate until the mixture reaches a temperature of 70° to 80° C. About 25 cc. more of the dilute acid are now added and the excess permanganate titrated in a hot (approx. 80° C.) solution with N/5 sodium oxalate. The $Na_2C_2O_4$ solution should be added, from a 25-cc. burette, cautiously allowing time for reaction with each addition. When the pink color fades the reading is taken. A drop of N/5 $KMnO_4$ should restore the pink color. Total permanganate taken minus the back titration with oxalate = cc. $KMnO_4$ required by the nitrite.

One cc. N/5 $KMnO_4$ = 0.0038 g. N_2O_3, or 0.0069 g. $NaNO_2$, or 0.0085 g. KNO_2.

THE ANALYSES OF OLEUM OR FUMING SULPHURIC ACID AND OF MIXED ACID

The analyses of fuming sulphuric acid and mixed acid are placed under one general scheme as the procedure for oleum is included in that of mixed acid. The term oleum is given to strong sulphuric acid containing free SO_3, the combined

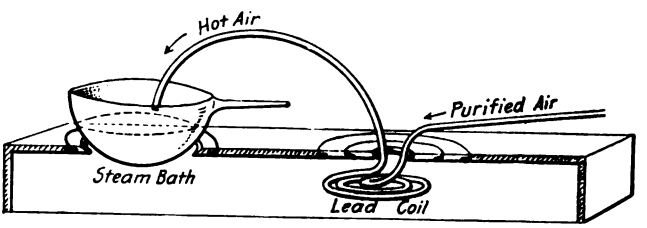

FIG. 84.—Method for Rapid Evaporation of Liquids.

water in the product decreasing (along with sulphuric acid) with the increase of free SO_3 or sulphuric anhydride. Mixed acid is the technical name for the mixture of strong sulphuric acid and nitric acid or of oleum and nitric anhydride, the product being commonly used in nitrating glycerine, cotton and other materials. The analysis includes the determinations of H_2SO_4, HNO_3, N_2O_5, N_2O_3 and in the case of oleum, the determination of SO_3. In the presence of the latter, HNO_3 is assumed to lose its combined water according to the reaction:

$$2HNO_3 + SO_3 = H_2SO_4 + N_2O_5$$

In absence of nitric acid SO_2 may be present. It is assumed that if HNO_3 is present the SO_2 is oxidized to SO_3 with formation of H_2SO_4 and the anhydrides SO_3 and N_2O_3 according to the reaction.

$$N_2O_5 + H_2O + 2SO_2 = N_2O_3 + SO_3 + H_2SO_4$$

Some chemists prefer to express the reaction:

$$2HNO_3 + SO_2 = H_2SO_4 + N_2O_4.$$

The analysis is carried out by three titrations—(*a*) determination of total acidity, (*b*) determination of sulphuric acid including SO_3 free in case of oleum, (*c*) determination of lower oxides.

For economy of time the following order should be observed: The sample for the determination of sulphuric acid and free SO_3 (oleum) should be weighed, diluted with water according to the detailed procedure and placed on the steam bath for evaporation. During the evaporation the titration for total acidity of the sample and the titration for the lower oxides are made and finally that of oleum on the evaporated sample.

Special Reagents.

Normal Sodium Hydroxide. One cc. = 0.04904 gram H_2SO_4.

Tenth Normal Potassium Permanganate. 3.16 grams $KMnO_4$ per liter. Standardized against N/10 solution of Sorensen's Sodium Oxalate. (See Preparation of Standard Reagents.) One cc. = 0.0019 gram N_2O_3, or 0.002351 gram HNO_2.

Procedure. Total Acids

The sample is accurately weighed by one of the procedures recommended for strong acids. The Dely weighing tube is excellent for this purpose. Such a weight being taken as will require a titration between 75 and 100 cc., e.g., containing an equivalent of 3.675 grams to 4.9 grams H_2SO_4. The acid is now run under cold CO_2 free water according to directions (above reference), and the acid titrated with N/1 solution of NaOH.

One cc. NaOH = 0.04904 g. H_2SO_4. Calculate to per cent $\frac{\text{cc. NaOH} \times .04904 \times 100}{\text{Weight of Acid Taken}}$.

Lower Oxides

Ten cc. of the sample, weighed in a pipette with capillary delivery tip, are cautiously run into about 400 cc. of cold water, keeping the delivery tip well under the water and in rapid motion to prevent overheating through local action. The mixture is titrated with N/10 $KMnO_4$ until a pink tint is obtained that does not fade in three minutes.

1 cc. N/10 $KMnO_4$ = 0.0019 g. N_2O_3. (N_2O_3 to N_2O_4 factor = 2.42.)

1 cc. N/10 $KMnO_4$ = 0.0046 g. N_2O_4.

1 cc. N/10 $KMnO_4$ = 0.00235 g. HNO_2. Equivalent H_2SO_4 = 0.0049043 g. per cc.

1 cc. N/10 $KMnO_4$ = 0.0032035 g. SO_2.

1 cc. N/10 $KMnO_4$ = 0.0041043 g. H_2SO_3.

NOTE. With exactly N/10 $KMnO_4$ on a 19-gram sample 1 cc. = 0.01% N_2O_3.

Sulphuric Acid and Free SO_3

The sample is weighed in a Dely tube and run under cold water, as in case of total acids, using in this case about 45 to 50 cc. of water in a 4-in. casserole. The solution is evaporated on the steam bath to expel the volatile acids, lower oxides and nitric. The evaporation is hastened by blowing a current of hot, dry, pure air over the sample. (Air purified by passing through a glass wool or asbestos dust filter. It is heated by passing it through a coil kept in the steam bath—see

cut.) About 5 cc. of water are added and this again evaporated off. The acid thus obtained is $H_2SO_4+SO_3$.

The acid is taken up with water and titrated with standard caustic, using CO_2 free water and phenolphthalein indicator.

One cc. N/1 NaOH = 0.004904 gram H_2SO_4.

Nitric Acid

This may be obtained from the above determinations according to calculations following. It may be obtained by direct titration with standard ferrous sulphate, by running a weighed amount of mixed acid into 100 cc. of cold sulphuric acid and titrating to a yellowish red tint. For the detailed procedure see Nitric Acid, page 515.

Calculation of Results.

A. Nitric Acid and SO_2 being Absent.

The total acidity is calculated to SO_3. Reference is made to the table for Oleum from which the per cent H_2SO_4 and free SO_3 are obtained.

Example. Suppose the total acidity in terms of SO_3 was found to be 84.2. The acid contains 86% H_2SO_4 and 14% free SO_3.

B. Nitric Acid Absent, SO_2 is Present in the Mixture.

Total SO_3. From total acidity as SO_3 subtract $SO_2 \times 1.25$ (i.e., equivalent SO_3).

Combined water. $100-(\text{total } SO_3+SO_2)=H_2O$.

Combined SO_3. $H_2O \times 4.4445 = SO_3$ equivalent or combined SO_3.

Free SO_3. Total SO_3 − combined SO_3 = free SO_3.

Sulphuric acid. Combined SO_3+H_2O.

Example. If SO_2 was found to be 2% and the total acidity in terms of SO_3 = 83.5%

Total $SO_3 = 83.5-(2\times1.25) = 81\%$.

Water $= 100-(81+2) = 17\%$.

Combined $SO_3 = 17\times4.4445 = 75.56\%$.

Free $SO_3 = 81-75.56 = 5.44\%$.

Sulphuric acid $= 75.56+17 = 92.56\%$.

Report

Sulphuric acid = 92.56%.

Free SO_3 = 5.44.

SO_2 = 2.00. Total 100.

C. Nitric Acid Present and SO_2 Absent.

Nitric acid in presence of free SO_3 is assumed to be the anhydride N_2O_5.

N_2O_5. From the total acidity is subtracted the acidity after evaporation, both being calculated to equivalent SO_3. The difference multiplied by 1.349 = per cent N_2O_5.

H_2O. Total SO_3 (after evaporation) + N_2O_5 subtracted from 100 = H_2O.

Combined SO_3. $H_2O \times 4.4445 = SO_3$ equivalent to H_2O.

Free SO_3. Combined SO_3 subtracted from total SO_3 = free SO_3.

Sulphuric acid. Combined $SO_3+H_2O=H_2SO_4$.

Example. If total acidity = 84% in terms of SO_3 and the total SO_3 (after evaporation) = 82%, then the difference $2\times1.349 = 2.698\%$ N_2O_5.

Water = 100 − (82 + 2.698) = 15.302%.
Combined SO_3 = 15.302 × 4.4445 = 68.01%.
Free SO_3 = 82 − 68.01 = 13.99%.
H_2SO_4 = 68.01 + 15.302 = 83.312%.

Report
H_2SO_4 = 83.312%.
Free SO_3 = 13.980%.
N_2O_5 = 2.698%.
Total 100.

D. N_2O_5 Required to be Reported as HNO_3, 96%.[1]

HNO_3, 96% = SO_3 equivalent (acid expelled by evaporation) × 1.64. 100 − per cent HNO_3 (96%) = Oleum. Total SO_3 in oleum = $\frac{100 \times \text{total } SO_3}{\text{per cent oleum}}$.

Reference to the oleum table will give the per cent free SO_3 in the oleum.

Example. Suppose total acidity in terms of SO_3 = 84% and the SO_3 after evaporation = 82%, then HNO_3, 96% = the difference = 2 × 1.64 = 3.28% HNO_3 96%).

Oleum = 100 − 3.28 = 96.72%.

Total SO_3 in oleum = 100 × 82 divided by 96.72 = 84.78.

From the oleum table 84.78 gives 17.10% free SO_3.

Report

Nitric acid, 96%	= 3.28%
Oleum	= 96.72%
Free SO_3	= 17.10%
Total SO_3	= 84.78%

The nitric acid and oleum make a total of 100.

Formulæ for Diluting or Strengthening Solutions.[2]

To dilute a solution with water:

(*a*) $\frac{DZ}{A} = X$; $Y = Z - X$; or (*b*) $\frac{A - DX}{D} = Y$.

To dilute a strong with a weaker liquid:

(*a*) $\frac{A - DZ}{A - B} = Y$; $X - Z = Y$; or (*b*) $\frac{A - DX}{D - B} = Y$.

To strengthen a weak with a stronger liquid:

(*a*) $\frac{D - AZ}{C - A} = X$; $Y = Z - X$; or (*b*) $\frac{D - AY}{C - D} = X$.

A = actual concentration of the solution that is to be corrected;
B = concentration of the diluting solution;
C = concentration of the strengthening solution;
D = desired concentration;
X = amount of the stronger solution to be added, taken or prepared;
Y = amount of weaker solution to be added or taken;
Z = amount of solution desired or given.

All data are in terms of weight of the constituents.

[1] This is the usual strength of the commercial concentrated acid.
[2] Compiled by J. B. Barnitt.

FUMING SULPHURIC ACID EQUIVALENTS

Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3	Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3
81.63	100.00	100	0	90.82	111.25	50	50
81.82	100.23	99	1	91.00	111.48	49	51
82.00	100.45	98	2	91.18	111.70	48	52
82.18	100.67	97	3	91.37	111.93	47	53
82.37	100.90	96	4	91.55	112.15	46	54
82.55	101.13	95	5	91.73	112.37	45	55
82.73	101.35	94	6	91.92	112.60	44	56
82.92	101.58	93	7	92.10	112.82	43	57
83.10	101.80	92	8	92.29	113.05	42	58
83.29	102.03	91	9	92.47	113.28	41	59
83.47	102.25	90	11	92.65	113.50	40	60
83.65	102.47	89	11	92.84	113.73	39	61
83.84	102.70	88	12	93.02	113.95	38	62
84.02	102.92	87	13	93.20	114.17	37	63
84.20	103.15	86	14	93.39	114.40	36	64
84.39	103.38	85	15	93.57	114.62	35	65
84.57	103.60	84	16	93.76	114.85	34	66
84.75	103.82	83	17	93.94	115.08	33	67
84.94	104.05	82	18	94.12	115.30	32	68
85.12	104.27	81	19	94.31	115.53	31	69
85.31	104.50	80	20	94.49	115.75	30	70
85.49	104.73	79	21	94.67	115.97	29	71
85.67	104.95	78	22	94.86	116.20	28	72
85.86	105.18	77	23	95.04	116.42	27	73
86.04	105.40	76	24	95.22	116.65	26	74
86.22	105.62	75	25	95.41	116.88	25	75
86.41	105.85	74	26	95.59	117.10	24	76
86.59	106.07	73	27	95.78	117.33	23	77
86.78	106.30	72	28	95.96	117.55	22	78
86.96	106.53	71	29	96.14	117.77	21	79
87.14	106.75	70	30	96.33	118.00	20	80
87.33	106.98	69	31	96.51	118.22	19	81
87.51	107.20	68	32	96.69	118.45	18	82
87.69	107.42	67	33	96.88	118.68	17	83
87.88	107.65	66	34	97.06	118.90	16	84
88.06	107.87	65	35	97.25	119.13	15	85
88.24	108.10	64	36	97.43	119.35	14	86
88.43	108.33	63	37	97.61	119.57	13	87
88.61	108.55	62	38	97.80	119.80	12	88
88.80	108.78	61	39	97.98	120.03	11	89
88.98	109.00	60	40	98.16	120.25	10	90
89.16	109.22	59	41	98.35	120.48	9	91
89.35	109.45	58	42	98.53	120.70	8	92
89.53	109.67	57	43	98.71	120.92	7	93
89.71	109.90	56	44	98.90	121.15	6	94
89.90	110.13	55	45	99.08	121.37	5	95
90.08	110.35	54	46	99.27	121.60	4	96
90.27	110.58	53	47	99.45	121.83	3	97
90.45	110.80	52	48	99.63	122.05	2	98
90.63	111.02	51	49	99.82	122.28	1	99
				100.00	122.50	0	100

Compiled from the table by H. B. Bishop, Van Nostrand's Chemical Annual, 1913

ANALYSIS OF ACETIC ACID

The acidity of acetic acid may be determined by titration with standard caustic, using phenolphthalein as indicator.

About 4 to 5 grams of glacial acetic acid or a corresponding amount of dilute acid are taken for analysis, being weighed out in a weighing bottle or other suitable container used for strong and weak acids. The acid is mixed with about 250 cc. of water and titrated in the presence of phenolphthalein indicator with normal caustic.

One cc. N/1 NaOH = 0.06003 gram CH_3COOH.

Impurities in Acetic Acid

The more important impurities that are looked for in commercial acetic acid are formic acid, furfurol, acetone, sulphuric acid, sulphurous acid, hydrochloric acid, metals.

In the examination of the acid the physical appearance—turbidity and color are noted.

Formic Acid in Acetic

Qualitative. Ten cc. of the acid (glacial diluted 1 : 10) are heated with 1 gram of sodium acetate and 5 cc. of 5 per cent mercuric chloride solution. A turbidity indicates formic acid.

Quantitative. Five grams of glacial acetic acid or corresponding quantity of dilute acid are treated with 5 grams of sodium acetate and 40 cc. of mercuric chloride solution (5 per cent) and 30 cc. of water added. The mixture is heated in a flask with a return condenser, the flask being surrounded by steam. The precipitated mercurous chloride, HgCl, is filtered off, dried and weighed.

Weight of HgCl × 0.0977 = formic acid equivalent.

Furfurol in Acetic Acid

Qualitative. Aniline dissolved in pure glacial acetic acid (5 cc. aniline in 2 cc. glacial acetic acid) and added to 100 cc. of the sample will produce a red color in presence of furfurol.

Quantitative. The test may be made quantitative by comparing the color produced with standard solutions containing known amounts of furfurol. One gram of redistilled furfurol is dissolved in 100 cc. of 95 per cent alcohol. 1 cc. of this solution is diluted to 100 cc. with 95 per cent alcohol. 1 cc. = 0.001 gram of the reagent.

Test for furfurol in vinegar. Fifty cc. of the vinegar is neutralized with sodium hydroxide, and 15 to 20 cc. are distilled. Two cc. of colorless aniline and 0.5 cc. of hydrochloric acid (1:12) added. The mixture is warmed to about 15° C. for a few minutes and the color compared with standards prepared in the same way.

Gravimetric Method with Phloroglucid

Place a quantity of the material, chosen so that the weight of phloroglucid obtained shall not exceed 0.300 gram, in a flask, together with 100 cc. of 12 per cent hydrochloric acid (specific gravity, 1.06), and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and so regulate as to distill over 30 cc. in about ten minutes, the distillate passing through a small filter paper. Replace the 30 cc. driven over by a like quantity of the dilute acid added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 cc. To the completed distillate gradually add a quantity of phloroglucol (purified if necessary) dissolved in 12 per cent hydrochloric acid and thoroughly stir the resulting mixture. The amount of phloroglucol used should be about double that of the furfural expected. The solution first turns yellow, then green, and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. Make the solution up to 400 cc. with 12 per cent hydrochloric acid, and allow to stand overnight.

Filter the amorphous black precipitate into a tared Gooch crucible through an asbestos felt, wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for four hours at the temperature of boiling water, cool and weigh, in a weighing bottle, the increase in weight being reckoned as phloroglucid. To calculate the furfural, pentose, or pentosan from the phloroglucid, use the following formulas given by Kröber:

(*a*) For weight of phloroglucid " a " under 0.03 gram.

$$\text{Furfural} = (a+0.0052)\times 0.5170.$$
$$\text{Pentoses} = (a+0.0052)\times 1.0170.$$
$$\text{Pentosans} = (a+0.0052)\times 0.8949.$$

(*b*) For weight of phloroglucid " a " over 0.300 gram.

$$\text{Furfural} = (a+0.0052)\times 0.5180.$$
$$\text{Pentoses} = (a+0.0052)\times 1.0026.$$
$$\text{Pentosans} = (a+0.0052)\times 0.8824.$$

For weight of phloroglucid " a " from 0.03 to 0.300 gram use Kröber's table or the following formulas:

$$\text{Furfural} = (a+0.0052)\times 0.5185.$$
$$\text{Pentoses} = (a+0.0052)\times 1.0075.$$
$$\text{Pentosans} = (a+0.0052)\times 0.8866.$$

The phloroglucol is purified by recrystallization from hydrochloric acid. For details of the procedure see Bulletin 107, U. S. Dept. of Agriculture, Bureau of Chemistry. (1912, page 54.)

Acetone in Acetic Acid

Fifteen grams of glacial acetic acid, or a corresponding amount of weak acid, is treated with 70 cc. potassium hydroxide (10 per cent solution), or sufficient caustic

to make the solution slightly alkaline. The solution is cooled and 25 cc. N/5 iodine solution added and sufficient hydrochloric acid to make the mixture faintly acid. The excess of iodine is titrated with N/5 sodium thiosulphate, using starch indicator. The total iodine solution taken minus the equivalent cc. of thiosulphate = the iodine combined with the acetone, then the weight of iodine in grams multiplied by 0.07612 = grams acetone in the sample.

Sulphuric Acid in Acetic Acid

This is best determined by the turbidity test. About 5 cc. of the sample are taken and 1 drop of hydrochloric acid and half a cc. of 10 per cent barium chloride. The turbidity is now compared with a standard pure acetic acid solution containing a known quantity of $BaSO_4$, the standard being added to a comparison cylinder until the turbidity is the same as that of the sample, which has been diluted to a convenient volume in a Nessler tube or similar comparison cylinder. The apparatus used in determining small amounts of titanium, lead, etc., is suitable for this test. In this case the glowing wire or filament of an incandescent light is viewed through the solutions, the brightness of the wire acting as a guide in matching the solutions.

Sulphurous Acid in Acetic Acid

This is best detected by placing in a small flask about 20 cc. of the sample, adding 5 cc. of strong hydrochloric acid and about 3 grams of zinc and covering with a filter paper saturated with lead acetate. The blackening of the paper indicates SO_2 in the sample (e.g., reduced to H_2S by the hydrogen generated by the zinc).

The sulphurous acid is best titrated with N/10 iodine solution, using starch indicator.

Hydrochloric Acid in Acetic Acid

Determined by the turbidity test as in case of sulphuric acid, silver nitrate solution being used to precipitate AgCl, and nitric acid substituted for hydrochloric acid.

Metals in Acetic Acid

Total Solids. Ten to 100 grams of the acid is evaporated to dryness in a platinum dish. The residue contains the non-volatile solids.

ACETATES

Two to 5 grams of the material is placed in a Kjeldahl flask connected by means of a condenser to a receiving flask containing half normal caustic. About 20 cc. of 85 per cent phosphoric acid are added and about 150 cc. of water. Gentle heat is applied and gradually increased. About 100 cc. of the solution is distilled into the caustic. Additional hot water is added to the residue in the Kjeldahl flask and the distillation continued. This is repeated until about 800 cc. of solution has been distilled over. The CO_2 is boiled out of the distillate, a reflux condenser being used to prevent loss of the acetic acid. If the solution is alkaline, a known

amount of acid is added and the CO_2 boiled out. The excess acid is now titrated and the amount of acetic acid in the distillate calculated.

One cc. N/2 NaOH = 0.030015 gram CH_3COOH.

$CH_3COOH \times 1.3169 = Ca(CH_3CO_2)_2$, or $\times 1.1.3663 = CH_3COONa$.

Acetates of the Alkalies and Alkaline Earths. In absence of other organic acids, nitrates, etc., a quick method is suggested by Sutton (Vol. Analy., X. Ed., p. 91). The salts are converted into carbonates by ignition and the residue titrated with normal acid.

One cc. N/1 acid = 0.06003 gram CH_3COOH.

CITRIC ACID

The free acid may be titrated with sodium hydroxide, using phenolphthalein indicator. One cc. N/1 alkali = 0.07 gram crystallized citric acid.

VOLUMETRIC ESTIMATION OF FREE ACID IN PRESENCE OF IRON SALTS

The red precipitate formed when solutions containing iron are titrated with caustic makes it difficult to detect the end-point of neutralization; the method suggested by C. A. Ahlum[1] takes advantage of the white compound formed by precipitating the iron as a phosphate and the fact that monosodium phosphate is neutral to methyl-orange indicator.

Reactions

$$Fe_2(SO_4)_3 + 2NaH_2PO_4 + x \text{ free acid} = 2FePO_4 + Na_2SO_4 + x \text{ free acid} + 2H_2SO_4,$$

or $$2FeCl_3 + 2NaH_2PO_4 + x \text{ free acid} = 2FePO_4 + 2NaCl + x \text{ free acid} + 4HCl.$$

The acid equivalent to ferric iron is deducted from the total acid found, the excess acid being due to the free acid in the solution.

Procedure. To the solution containing the iron and free acid is added an excess of C.P. solution of monosodium phosphate (neutral to methyl-orange), and then a few drops of the indicator. The acidity of the solution is now determined by titration with standard caustic in the usual way, the solution being cold. From this titration the total free and combined acid are calculated.

Iron is now determined in a separate portion by titration with stannous chloride or dichromate.

Calculation.

(A) $Fe_2O_3 \times 1.2285$ = g. H_2SO_4 (combined). $Fe_2O_3 \times 0.9135$ = g. HCl (combined).

(B) One cc. N/5 NaOH = .00981 gram H_2SO_4 or .00729 gram HCl.

Total acid (B) minus combined acid (A) = *free acid*.

[1] C. A. Ahlum, The Analyst, **31**, 168, 1906.

ESTIMATION OF THE CARBONATES AND HYDRATES OF POTASSIUM AND SODIUM WHEN TOGETHER IN SOLUTION[1]

Procedure. A measured volume of the solution is titrated, using phenolphthalein as indicator. The acid used is equivalent to all of the hydrate and half the carbonate; methyl orange is now added and the titration completed; the additional amount of the acid used is equivalent to half the carbonate, therefore the amount of acid required for the carbonates and for the hydrates can be calculated from these figures.

The fully neutralized solution is evaporated to dryness and the residue weighed. The result is the weight of the mixed sulphates, due to the carbonates and hydrates of potassium and soda in the solution.

Calculate the total acid required to its equivalent of potassium sulphate, subtract from this result the weight of the mixed sulphates, and the difference is due to the sodium sulphate in the mixed sulphates, owing to the difference in the molecular weights of potassium sulphate and sodium sulphate. The whole of the acid used has been calculated to potassium sulphate, and as the acid was neutralized by carbonates and hydrates, it is evident the proportion of total sulphate, due to the carbonates and hydrates, is equivalent to the amount of the acid used for each respectively; therefore the proportion of the above obtained difference due to the carbonates and the hydrates respectively is also proportional to the amount of acid used for each.

Example. A solution of the mixed carbonates and hydrates of potassium and sodium required:

(40 cc. NaOH : 40 cc. KOH) 80 cc. of acid to neutralize the hydrates.

(10 cc. Na_2CO_3 : 10 cc. K_2CO_3) 20 cc. of acid to neutralize the carbonates.

100 cc. total acid required to neutralize the solution.

Total acid 100 cc. calculated to K_2SO_4 = 0.87 gram.

Total neutralized solution evaporated to dryness ($K_2SO_4 + Na_2SO_4$) = 0.79 gram.

Difference due to Na_2SO_4 in weighed sulphates = 0.08 gram.

($K_2SO_4 - Na_2SO_4$) : Na_2SO_4 : : Diff :
32 : 142 : : 0.08 : 0.355 Na_2SO_4 present in the mixed sulphates.

And the mixed sulphates 0.79 gram $- 0.355 = 0.435$ K_2SO_4 present in the mixed sulphates.

Therefore the mixed sulphates consist of Na_2SO_4 0.355 gram, K_2SO_4 0.435 gram.

The proportion of the acid used for the hydrates is 80/100 and for the carbonates is 20/100.

Therefore the proportion of the difference (0.08) due to Na_2SO_4 from the hydrate NaOH is $0.08 \times 80/100 = 0.064$. For the carbonates $= 0.08 \times 20/100 = 0.016$.

By the above ratios 32 : 142 : : 0.064 : 0.284 Na_2SO_4 from NaOH = 40 cc. N/10 acid. 32 : 142 : : 0.016 : 0.071 Na_2SO_4 from Na_2CO = 10 cc. acid.

[1] W. A. Bradbury and F. Owen. C. N., **107**, 2778, 85 (Feb. 21, 1913).

80 cc. acid used for the hydrates $= 0.696$ K_2SO_4.
0.284 Na_2SO_4 from the NaOH $= 0.348$ K_2SO_4.
Difference $= K_2SO_4$ from KOH $= 0.348 = 40$ cc. N/10 acid.
20 cc. acid used for the carbonates $= 0.174$.
0.071 Na_2SO_4 from the Na_2CO_3 $= 0.087$.
Difference $= K_2SO_4$ from K_2CO_3 $= 0.087 = 10$ cc. acid.

The figures correspond with the quantities taken.

80 cc. of acid to neutralize the hydrates.
20 cc. of acid to neutralize the carbonates.

$Na_2SO_4 = 0.355$ { NaOH 0.284 = 40 cc. acid; Na_2CO_3 0.071 = 10 cc. acid } 80 cc. acid.

$K_2SO_4 = 0.435$ { KOH 0.348 = 40 cc. acid; K_2CO_3 0.087 = 10 cc. acid } 20 cc. acid

Totals 0.790 0.790(a)100

Calculate these sulphates to the corresponding hydrates and carbonates.

The author acknowledges the assistance rendered by Mr. J. P. Kelly and B. Clark by review and criticism of this chapter.

WATER ANALYSIS

D. K. FRENCH

Probably at no other time has the importance of a water supply, either for domestic or industrial purposes, been so great, as in these early years of the twentieth century. The increasing realization of the effect of contaminating materials, both organic and inorganic, on a municipal or private drinking supply—and history's record of the devastating nature of epidemics due to water-borne disease organisms, have led to the careful investigation of water for its sanitary value and the development of materials and equipment to fight and eliminate such contamination, and have increased many hundreds of per cent the factor of safety to the public health. In like manner, and even to a greater extent, has the value of water for industrial uses been a matter for careful consideration. It is hard for the public to realize the immense quantities of water used for industrial purposes, not only for the development of steam and electric power, but also for purposes of manufacture.

From the standpoint of power development we are familiar with the heat losses and the increased operating expenses due to scale formation in the steam or locomotive boiler, and also to the continued rapid decrease in valuation of boiler property, or of power plant property, due to corrosion or rusting. Another element of trouble which is noticed not so much in stationary boiler practice as in locomotive boiler practice, is the element of foaming and priming of a water, which results in much more rapidly putting the steam raiser out of active service than either of the other types of trouble.

From the standpoint of plant deterioration due to rusting and corrosion one has only to look to the great mass of works on the corrosion of iron and steel which are largely results of the growing need for some information as to the cause and possible prevention of this particular phase of trouble.

Little work has been done so far on the actual theory of foaming troubles in water, although Mr. Stabler of the United States Geological Survey considers it quite thoroughly in several Government bulletins with which he has been connected.[1]

In the world of industry the action of a hard water upon soap consumption has been known for centuries, and for a considerable period of time the value of a water was determined largely by the amount of soap that it would consume and render insoluble. This same hardness has a noticeable effect in the textile industry, in bleaching and dyeing, in the canning industry, especially when the water supply contains such substances in large quantities. In the photographic industry the presence of chlorides in water and certain alkalies is a source of considerable trouble, and in every case, before any intelligent effort can be made to overcome these troubles, a complete analysis of the water is necessary.

It shall be our purpose in the methods which follow to give, where it is possible, first a system of analysis whereby a complete analysis can be made, and to follow

[1] Water Supply Paper 274 and 254 (Supplement).

80 cc. acid used for the hydrates $= 0.696$ K_2SO_4.
0.284 Na_2SO_4 from the NaOH $= 0.348$ K_2SO_4.
Difference $= K_2SO_4$ from KOH $= 0.348 = 40$ cc. N/10 acid.
20 cc. acid used for the carbonates $= 0.174$.
0.071 Na_2SO_4 from the Na_2CO_3 $= 0.087$.
Difference $= K_2SO_4$ from K_2CO_3 $= 0.087 = 10$ cc. acid.

The figures correspond with the quantities taken.

80 cc. of acid to neutralize the hydrates.
20 cc. of acid to neutralize the carbonates.

$Na_2SO_4 = 0.355$ { NaOH 0.284 = 40 cc. acid; Na_2CO_3 0.071 = 10 cc. acid } 80 cc. acid.

$K_2SO_4 = 0.435$ { KOH 0.348 = 40 cc. acid; K_2CO_3 0.087 = 10 cc. acid } 20 cc. acid

Totals 0.790 0.790(a)100

Calculate these sulphates to the corresponding hydrates and carbonates.

The author acknowledges the assistance rendered by Mr. J. P. Kelly and B. F. Clark by review and criticism of this chapter.

1.246 grams potassium platinic chloride ($PtCl_4 2KCl$)[1] containing 0.5 gram of platinum and 1 gram crystallized cobalt chloride ($CoCl_2 6H_2O$) containing 0.25 gram cobalt (Co), are dissolved in water with 100 cc. hydrochloric acid and made to one liter with distilled water. This solution is diluted with distilled water for comparative purposes, but a water with a color greater than 70 should be diluted prior to comparison. The standards for observation should be in 100-cc. Nessler tubes with the mark 20–25 cm. above the bottom and should be viewed vertically downwards to a white reflective surface.

Standard glass disks are used by the United States Geological Survey [2] in place of the above standard.

Odor. Observations should be made both on cold and hot samples. Note should be made immediately on opening containers as some odors are very transient and rapidly disappear.

Cold. Shake sample violently in collecting bottle, same to be about half full. Remove glass stopper and smell at neck of bottle.

Hot. Use either open beaker, 400 cc., containing 150 cc. sample well covered and heated nearly to boiling, or sealed glass stoppered bottle or saponification flask, heating fifteen minutes just under boiling. Allow to cool slightly, remove stopper, shake and smell. Designate odor as aromatic, grassy, earthy, musty, fishy, putrid, disagreeable, peaty, sweetish, etc. The following table expressing intensity of odor is copied from the American Public Health Association Standard Methods, 1913, p. 12:

Numerical Value.	Term.	Approximate Definition.
0	None.	No odor perceptible.
1	Very Faint.	An odor that would not be detected ordinarily by the average consumer, but that could be detected in the laboratory by an experienced observer.
2	Faint.	An odor that the consumer might detect if his attention were called to it, but that would not attract attention otherwise.
3	Distinct.	An odor that would be detected readily and that might cause the water to be regarded with disfavor.
4	Decided.	An odor that would force itself upon the attention that might make the water unpalatable.
5	Very Strong.	An odor of such intensity that the water would be absolutely unfit to drink. A term to be used only in extreme cases.

Taste. May be made on hot and cold samples. A simple statement following largely the terms applied to odor in expressing results, brackish, astringent, salty, sweetish, etc.

[1] Care should be taken that this be the bright yellow platinic salt, and not contaminated with the reddish platinous salt.

[2] App. made by Builders' Iron Foundry, Providence, R. I.

CHEMICAL TESTS

Free Ammonia

Apparatus. The apparatus for this determination should be as far as pc sible free from joints or connections that are subject in any way to outsi

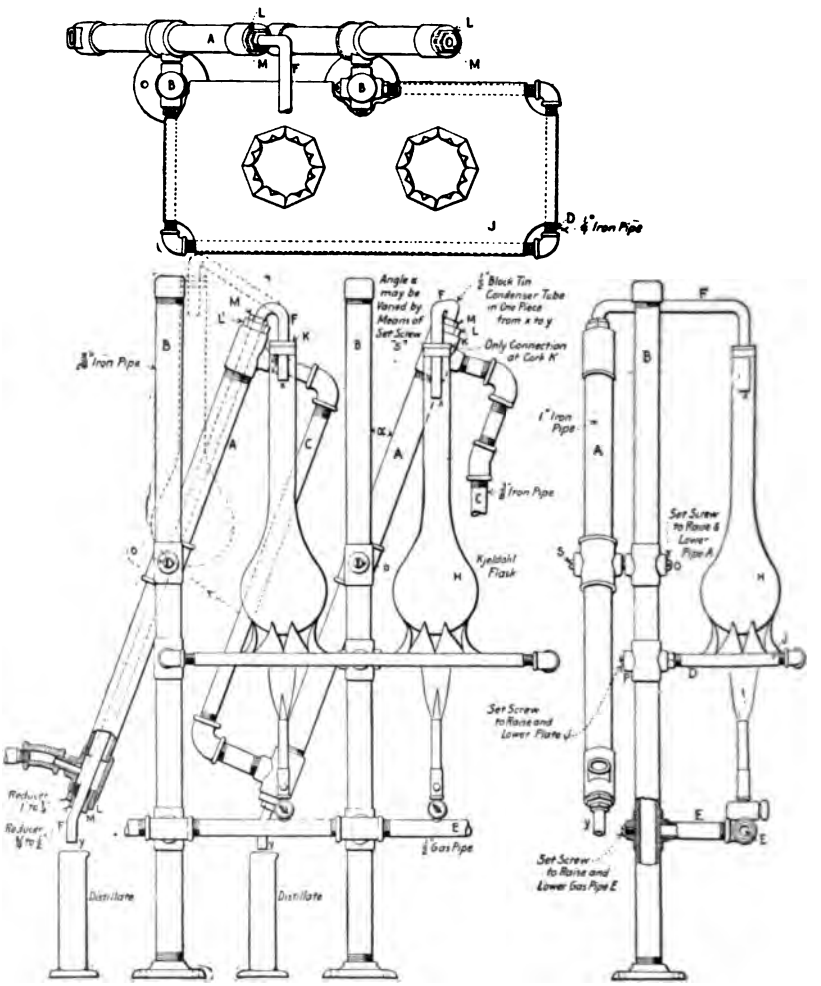
Angle α may be Varied by Means of Set Screw S
Only Connection at Cork K
Kjeldahl Flask
Set Screw to Raise and Lower Flask J
Set Screw to Raise & Lower Pipe A
Set Screw to Raise and Lower Gas Pipe E
Distillate
Distillate

FIG. 85.

contamination or to decomposition. The apparatus is composed of a distillatic flask and a condenser, with possibly a safety tube located somewhere near the fla to avoid the possible carrying over of impurities in connection with the stea

Reagents. 1. ***Ammonia-free Water.***

2. ***Standard Ammonium Chloride Solution.*** Dissolve 3.82 grams of ammonium chloride in 1 liter of distilled water. Dilute 10 cc. of this to 1 liter with ammonia-free water. 1 cc. = 0.00001 gram of nitrogen.

3. ***Nessler's Solution.*** Dissolve 50 grams of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride until a faint show of excess is indicated. Add 400 cc. of 50% solution of potassium hydrate. After same has clarified by sedimentation, make up to 1 liter with water, allow to settle and decant.

Optional Method. Dissolve 61.75 grams of potassium iodide in 250 cc. of redistilled water, and add a cold solution of mercuric chloride which has been saturated by boiling with excess of salt. Pour in the mercury solution cautiously, and add an amount just sufficient to make the color a permanent bright red. With a little practice the exact depth of color can be easily duplicated. It will take a little over 400 cc. of the mercuric chloride solution to reach this end-point. Dissolve the red precipitate by adding exactly .75 gram of potassium iodide. Then add 150 grams of potassium hydrate dissolved in 250 cc. of water. Make up to 1 liter. Mix thoroughly and allow the precipitate formed to settle. Pour off the supernatant liquid. Mercuric chloride increases the sensitiveness and potassium iodide decreases it.

Operation. Clean apparatus thoroughly as follows:

Fill a flask, which for most satisfactory results should be an 800-cc. Kjeldahl flask, with 500 cc. of distilled water. Add a pinch of c.p. sodium carbonate and distill first of all with no running water in the condenser jacket until free steam blows through the apparatus. Then turn on condenser water and distill off approximately 250 cc., testing the last 50 cc. with Nessler's solution, and this portion should not show color in fifteen minutes' time. The flask is then emptied of the remaining water, 500 cc. of the water to be analyzed placed therein, and if acid, neutralized with c.p. sodium carbonate. A slight excess hurries the ammonia liberation but also tends to cause bumping. The distillation is then started, distilling 6 cc. to 10 cc. per minute, and three separate portions of 50 cc. each are caught in Nessler jars. After 150 cc. is distilled the flame should be removed. To each 50-cc. portion add 2 cc. Nessler's solution and after ten minutes' standing compare with standards from the standard ammonium chloride solution.

Albuminoid Ammonia

Reagent. 1. ***Alkaline Potassium Permanganate.*** Dissolve 200 grams of potassium hydrate and 8 grams c.p. potassium permanganate in 1250 cc. of water, boil down to 1 liter and bottle while still warm.

Operation. Add 50 cc. alkaline potassium permanganate solution and several pieces of washed and ignited pumice to the water remaining in the flask from the free ammonia determination and continue the distillation, taking off four or five separate portions of 50 cc. each in Nessler jars. Add 2 cc. Nessler's solution to each and after ten minutes standing compare color with standard as in the free ammonia determination.

Organic Nitrogen

While this determination is not usually made we give it for the sake of completeness.

The portion of sample from the free ammonia determination, or a new portion freed from free ammonia by distillation, is acidified with 5 cc. C.P. sulphuric

acid (nitrogen-free) and digested in a hood until colorless and H_2SO_4 fumes are given off. A little ignited pumice will guard against bumping. Remove from flame, add potassium permanganate in small portions until a heavy greenish precipitate persists, cool, dilute with ammonia-free water, neutralize with 10% Na_2CO_3 solution (NH_3 free), distill into Nessler tubes and compare as in free and albuminoid ammonia.

Permanent standards [1] can be made using potassium platinic chloride, 2 grams dissolved in water, 100 cc. strong hydrochloric acid and made to 1 liter; and cobalt solution, 12 grams cobaltous chloride ($CoCl_2\ 6H_2O$) dissolved in distilled water, 100 cc. strong hydrochloric acid added and made to 1 liter. The following table represents the amounts used, to be made to 50 cc. with distilled water in Nessler tubes for comparison, the 150-cc. mark being 20–25 cm. above the bottom, but should be checked against Nesslerized standards and the Nessler solution modified, if necessary, until the standards agree. This is accomplished by varying the amounts of potassium iodide and mercuric chloride.

Equivalent Volume of Standard Ammonium Chloride, cc.	Platinum Solution, cc.	Cobalt Solution, cc.
0.0	1.2	0.0
0.1	1.8	0.0
0.2	2.8	0.0
0.4	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	17.3	4.5
3.5	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7
5.0	20.0	10.4
6.0	20.0	15.0
7.0	20.0	22.0

Nitrogen as Nitrite

Reagent. 1. ***Sulphanilic Acid.*** Dissolve 8 grams of the acid in 1 liter of acetic acid, specific gravity 1.04. This is practically a saturated solution and keeps well.

2. ***Naphthylamine Acetate.*** Dissolve 5 grams of α-naphthylamine in 1 liter of acetic acid, specific gravity 1.04, and filter through absorbent cotton (previously washed).

NOTE. A slightly pink color resulting on standing does not materially interfere with the use of this solution.

3. ***Sodium Nitrite Solution.*** Dissolve 1.1 grams of silver nitrite in nitrite-free water. Precipitate the silver with sodium or potassium chloride solution and dilute

[1] Permanent Standards (Jackson, Tech. Quart., 1900, vol. 13, p. 320.)

to 1 liter. Dilute 100 cc. of this solution to 1 liter and then 10 cc. of this second solution to 1 liter with sterilized nitrite-free water, adding 1 cc. of chloroform and holding in a sterilized bottle. 1 cc. = 0.0001 milligram of nitrogen.

Operation. Take 100 cc. of the water after filtration and clarification, preferably with aluminum hydrate, to remove possible suspended iron and material which might interfere with color production. Add 2 cc. each of solutions No. 1 and No. 2. After ten minutes' standing compare with standards made up from the standard sodium nitrite solution (No. 3).

Permanent Standards

Cobalt Solution. Dissolve 24 grams of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in distilled water, add 100 cc. of strong hydrochloric acid and make up to one liter with distilled water.

Copper Solution. Dissolve 12 grams of dry cupric chloride ($CuCl_2 \cdot 2H_2O$) in distilled water, add 100 cc. of strong hydrochloric acid and make up to one liter with distilled water.

The standards are used in 100-cc. tubes with the mark 12–14 cm. above the bottom. The following table gives the proportions of each solution to be made up to 100 cc.:

cc. Cobalt Solution.	cc. Copper Solution.	p.p.m. Nitrite per 100 cc. of Water.
.0	.0	.000
1.1	1.1	.001
3.5	3.0	.003
6.0	5.0	.005
12.5	8.0	.010

The solutions to use for 100 cc. of water are the old ones, as follows: 1 cc. of hydrochloric acid (1 : 4), 2 cc. of sulphanilic acid (8 grams per liter), and finally 2 cc. of naphthylamine hydrochloride (8 grams per liter with 10 cc. of strong hydrochloric acid), and allow color to develop twenty minutes.

NOTE. Volume 28, page 742, J. Soc. Chem. Ind., calls attention to the possibility of a permanent standard composed of a solution of acid magenta (fuchsine-S, acid fuchsine according to Weigert). According to this article, 0.2 of a gram of this dye is dissolved in 50 cc. of 2/N HCl and made up to 2000 cc. with distilled water. Of this solution 200 cc. are mixed with 50 cc. of 2/N HCl and again diluted to 2000 cc. with distilled water. From this latter solution standard solutions can be prepared containing various quantities, these standards being made up to 200 cc. with distilled water after the addition of 5 cc. of 2/N HCl. Considerable work is being done on this, but the standards have not yet been accepted in this country. However, standards can be made by matching these solutions against standards prepared in the usual way and their permanence is much greater than such standards.

Nitrogen as Nitrate

Phenolsulphonic Acid Method

Reagent. 1. ***Phenolsulphonic Acid.*** Dissolve 25 grams of pure white phenol in 150 cc. of pure concentrated sulphuric acid, add 75 cc. of fuming sulphuric acid (13% SO_3), stir well and heat for two hours at about 100°.[1]

[1] Jour. Amer. Chem. Soc., **33**, 382, 1911.

2. ***Ammonium Hydrate*** 1-1.

3. ***Sodium Carbonate.*** 10% solution of anhydrous Na_2CO_3.

4. ***Standard Nitrate Solution.*** Dissolve 0.72 gram pure or C. P. potassium nitrate in 1 liter of distilled water. Evaporate carefully 10 cc. of this solution on water bath, moisten thoroughly with 2 cc. of solution No. 1 and dilute to 1 liter. 1 cc. of this = 0.001 milligram of nitrogen.

Determination. Carefully evaporate 100 cc. of water after the addition of 2 cc. of sodium carbonate solution. After this evaporate to dryness, cool and add 2 cc. phenolsulphonic acid (No. 1), mixing well with a glass rod. Dilute with 25 cc. of distilled water and add an excess of ammonium hydrate, making up to 100 cc. volume with distilled water.

The dilute solution is then compared with the standard solution.

NOTES. When the chlorides are over 100 parts per million in the original sample they should be removed with the addition of silver sulphate in the solid form and the water should be filtered prior to evaporation. It is for this reason that ammonium hydrate is used to develop the color instead of potassium hydrate, which is frequently recommended, as a slight excess of silver sulphate will result in a dirty precipitate when using potassium hydrate, whereas the use of ammonia has no effect. Furthermore, the filtration of a turbid nitrate solution does not result in a satisfactory color, as would be the case without filtration.

Permanent standards can be made by procedure given on page 539, or standards can be made using tripotassium nitrophenoldisulphonate. The following method is given in an article in the J. Amer. Chem. Soc., Vol. 33, pp. 381-384:

The theoretical amount of powdered potassium nitrate is added to the disulphonic acid regent in small pinches at a time (for each cc. of reagent 0.1076 gram KNO_3), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate to a deep yellow color, filtered and the precipitate washed with boiling water to remove the barium salts which is but slightly soluble in cold water. This extraction must be thorough. Filtrates and washings are united, the barium removed by the addition of potassium carbonate until alkaline, the solution filtered and the filtrate concentrated and crystallized. The solution may then be easily purified by crystallization. In preparing the standards, however, solutions made from known amounts of nitrate standards will match up with this recrystallized solution, and by means of proper dilutions the series of standards can be made. Standards made this way will last for many months, whereas standards made from the standard nitrate solution are apt to lose value in a month's period and should be made up very frequently.

Optional Method—Aluminum Reduction [1]

Reagents. 1. ***Sodium or Potassium Hydrate Solution.*** Dissolve 250 grams of the hydrate in 1250 cc. of distilled water, add several strips of aluminum foil and allow action to pass overnight. Boil down to 1 liter.

2. ***Aluminum Foil.*** Use strips of pure aluminum approximately 10 cm. long, 9 mm. wide, and $\frac{1}{3}$ mm. thick, same to weigh about $\frac{1}{2}$ gram.

Operation. 100 cc. of water is placed in a 300-cc. casserole. Add 2 cc. of the hydrate solution and boil down to about 20 cc. Pour the contents of the casserole into a test-tube about 6 cm. long and 3 cm. in diameter and of approximately 100-cc. capacity. Rinse the casserole several times with nitrogen-free water and add the rinse water to that already in the tube, thus making the contents of the tube approximately 75 cc. Add a strip of aluminum foil. Close the tube by means of a rubber stopper through which passes a A-shaped glass tube about 5 mm. in diameter. Make the short end of the tube flush with the lower side of the

[1] Univ. of Illinois Bull. Water Survey, Series 7, p. 14, 1909; Amer. Jour. Pub. Hygiene, 19, 536, 1909.

rubber stopper while the other end extends below the surface of distilled water contained in another test-tube. This apparatus serves as a trap through which the evolved hydrogen escapes freely. The amount of ammonia escaping into the trap is slight and may be neglected. Allow the action to proceed for a minimum period of four hours, or overnight. Pour contents of the tube into a distilling flask, dilute with 250 cc. of ammonia-free water, distill and collect in Nessler tubes and Nesslerize. When the nitrate content is high, collect the distillate in a 200-cc. flask and Nesslerize an aliquot portion. If the supernatant liquid in the reduction tube is clear and colorless, the solution may be diluted to a definite volume and an aliquot part Nesslerized without distillation.

NOTE. Where the nitrates are very high, from 50 parts per million up, note additional method given under the head of Nitrate Determination in Mineral Analysis of Water.

Oxygen Consumed

Reagents. 1. ***Standard Potassium Permanganate Solution.*** Dissolve 0.4 gram C.P. salt in 1 liter of distilled water. 1 cc. is equivalent to 0.1 milligram available oxygen.

2. ***Standard Ammonium Oxalate Solution.*** Dissolve 0.888 gram C.P. ammonium oxalate in 1 liter of distilled water. 1 cc. is equivalent to 0.1 milligram of oxygen. The standard permanganate solution must be standardized against the ammonium oxalate solution.

3. ***Dilute Sulphuric Acid 1–3.***

Operation. 100 cc. of water are measured into a 450-cc. Erlenmeyer flask, acidified with 5 cc. dilute sulphuric acid. Ten cc. of standard permanganate solution is run in from a burette and the flask is placed in a bath of boiling water, the level of which is above the level of the flask contents, for thirty minutes. Remove. Add 10 cc. of standard oxalic solution and then determine the excess with the standard permanganate solution. Deduct from the total permanganate solution used the 10 cc. of oxalic acid, and the remainder represents oxygen consumed. For particularly bad waters smaller quantities of the sample are taken and diluted to 100 cc., as it is undesirable at any time in the course of boiling that the pink color of permanganate be completely discharged.

Chlorine as Chlorides

Reagents. ***Standard Salt Solution.*** 16.48 grams fused C.P. sodium chloride are dissolved in 1 liter of distilled water. 100 cc. of this solution diluted to 1 liter gives a standard solution, each cc. of which contains .001 gram of chlorine.

Standard Silver Nitrate Solution. 4.8 grams dried silver nitrate crystals are dissolved in one liter of distilled water. Each cc. of this solution is equivalent to approximately .001 gram of chlorine, standardized against the Standard Salt Solution.

NOTE. N/50 solutions of both sodium chloride and silver nitrate can be used where it is inconvenient to make too many standard solutions, using the proper factors.

Potassium Chromate. Ten per cent solution neutral potassium chromate.

NOTE. A. P. H. A., page 43, recommends 5 per cent solution of neutral potassium chromate, adding after solution of the crystals in a few cc. of water, sufficient silver nitrate to produce a slight red precipitation. This is filtered off, and the filtrate made up to volume.

Operation. 100 cc. of the sample are titrated with silver nitrate solution, using 1 cc. of the potassium chromate as indicator to the first persistence of the silver chromate red. Subtract 0.2 cc. blank from the reading. A white porcelain dish or casserole is the preferable container, although a flint-glass beaker over a white porcelain plate may be used. Where a chlorine is high and more than 15 cc. of silver nitrate is used, a smaller sample (50 cc. or 25 cc.) should be taken and distilled water added to bring the volume up to approximately 100 cc. If the original water is noticeably colored, 25 to 30 by standard, it may be decolorized by adding precipitated aluminum hydrate, bringing to a boil and filtering. Titration must always be made in the cold, however.

NOTE. Precipitated aluminum hydrate is prepared by dissolving potash alum in water, precipitating by adding carefully ammonia and washing in a large jar with distilled water, by decantation, until free from chlorine, ammonia, and nitrites. An acid water should first be neutralized with sodium carbonate and a water containing free hydrates should be neutralized with sulphuric acid. Where specially accurate work is desired, observations may be made in a dark room with a yellow light. (A. P. H. A., page 44.) A yellow photographic glass may be used in daylight and at night the ordinary carbon filament electric light.

Total Solid Residue

Evaporate 50 cc. to dryness, in a platinum dish, at about 270° Fahr., and bake for at least 30 minutes at that temperature. An ordinary water-bath temperature will not remove water of crystallization from ordinary sulphate or calcium sulphate. Where water is high in magnesium salts, as determined in mineral analysis, the water-bath temperature is more satisfactory, due to the readiness with which magnesium chloride and frequently magnesium carbonate will decompose to oxide. As a rule, however, a temperature from 240° to 270° meets most of the conditions.

Weight to tenths of milligram times 1168 = grs. per gal. total solids.
Weight to tenths of milligram times 20,000 = parts per million total solids.

Residues from acid waters should be ignited to a dull red heat after addition of a drop or so of sulphuric acid, to insure complete removal of the acid itself, which will not go off at the temperature stated. This will result in the decomposition of all iron compounds to the oxide form, and will fix all salts, lime, magnesium, sodium and potassium, in the sulphate form, and correction should be made for chlorides present, which would be converted into sulphate.

Waters high in magnesium salts should be evaporated at the first specified temperature, adding, however, a few cc. of 50 normal sodium carbonate solution to insure a slight excess of sodium carbonate, correcting for the weight of sodium carbonate added. Where the waters contain much organic matter after weighing, they may be very gently ignited at a very dull red heat until the carbon has been burned off. After cooling, the residue may be recarbonated with tested ammonia carbonate solution, and again dried in the usual way. The difference in weight after titrating for possible loss of chlorides, due to volatilization, gives a close approximation of the organic matter present. Similarly, waters high in magnesium chloride or nitrate compounds may be evaporated with a few drops excess of sulphuric acid, and ignited to a dull red heat, the residue being compared, where a complete analysis is made, with the sum of all bases calculated to the sulphate form. This is sometimes more convenient and satisfactory than the evaporation with excess sodium carbonate.

INTERPRETATION OF RESULTS

The interpretation of the results of a sanitary water analysis is largely a matter of experience, and it is impossible to lay down hard and fast rules covering this one matter. It is, however, possible to sum up the meanings of the various determinations made, as each determination has some bearing upon the sanitary condition.

In physical data the turbidity refers to insoluble matter in suspension. In many cases it is perfectly harmless, although less attractive, and frequently suggests contamination, which is as apt to be present as not. High turbidities, following rain storms or lake over-turnings, are usually accompanied by B. coli, the intestinal organism, in considerable quantity. The turbid waters of the West may cause stomach trouble until a person is accustomed to them. Color is due, usually, to an extract of vegetable or organic matter, or to iron salts, and in itself has no value save suggesting organic contamination. Highly colored water may have an astringent taste, and is not looked upon with favor by the consumer. It may cause corrosion in pipes and boilers.

Various organic matters are in no way determined in this analysis, the results obtained being simply indications of certain cycles in decomposition of nitrogenous material, as no decomposition can take place without some resulting nitrogen compound. Free ammonia represents the first stage in this decomposition, and represents the amount of organic matter present in a partially decomposed and decomposing state. Deep wells in glacial drift frequently also contain high ammonia, however, which would in no way suggest active contamination.

Albuminoid ammonia represents organic substances in an undecomposed state, which will, however, decompose under the proper conditions. The presence of nitrogen in such combination in large amount usually suggests the presence of pollution of a sewage character. However, its presence usually accompanies and varies in amount with the color and with the microscopic organisms.

The next stage in the cycle is nitrogen as nitrites, indicating that decomposition is actively progressing. Nitrite in surface water may indicate contamination when in considerable quantity, but in ground water is absolutely of no significance. (Proc. Am. W. W. Assoc., 1908, page 323.) Its presence is due to the action of certain types of bacteria either as a product of oxidation from free ammonia or as a product of reduction from nitrate. Ferrous compounds have also a bearing on such reduction.

The final state of decomposition is nitrogen as nitrate. This indicates the fact that at some time in the past organic matter has been present. Its presence indicates a purified water. In large amounts it may cause itching in sensitive persons. It is an important cause of corrosion in pipes and boilers.

The oxygen consumed represents the amount of oxygen required to oxidize organic matter already in the water. It has a bearing upon the organic matter, but there are many inorganic substances which also discharge the color of the permanganate solution, and the result should always be considered in the presence of the other determinations.

Chlorine as chlorides, if above the normal figure for any definite location, is a fairly good indication of sewage, as it is one of the most constant and principal constituents of sewage.

The total residue itself should not be too high, as an excess of inorganic

materials would stamp the water unfit from an industrial point of view, and also, from the standpoint of the individual, might make it unsatisfactory as a drinking supply, for daily consumption.

With reference to standards of purity, it is impossible to make absolute standards. We quote as a matter of interest a table published by the State of Illinois, giving their suggested limits of impurities for supplies in that State. (The remarks which follow are those of the State Geological Survey.)

	Lake Michigan.	Streams.	Springs and Shallow Wells.	Deep Drift Wells.	Deep Rock Wells.
Turbidity	None	10.	None	None	None
Color	None	.2*	None	None	None
Odor	None	None	None	None	None
Residue on Evaporation	150.	300.	500.	500.	500.
Chlorine	4.5	6.	15.	15.	5.-100
Oxygen consumed	1.6	5.	2.	2.-5	2.-5
Nitrogen as:					
Free Ammonia	.01	.05	.02	.02-3	.02-3
Albuminoid Ammonia	.08	.15	.05	.20	.15
Nitrites	.000	.000	.000	.005	.000
Nitrates	.04	.5	2.00	.50	.5
Alkalinity	120.	200.	300.	300.	300.
Bacteria per cc	100.	500.	500.	100.	100.
Colon bacillus in one cc	Absent	Absent	Absent	Absent	Absent

*Modified Nessler or Natural Water Standard equal 26 p.p.m. platinum scale.

The formation of a reasonable and just opinion regarding the wholesomeness of a water requires that there be taken into consideration all the data of the analysis, together with the history of the water; the nature of the source; character of the soil and earth or rock strata, and the surroundings. The interpretation of results is a task for the expert.

Chlorine is the most permanent element shown in water analysis, as it is never removed from water by any changes or processes of purification. Salt deposits, however, in the soil must also be taken into consideration.

MINERAL ANALYSIS

Outline of Procedure

50 cc. (Certified pipette or burette) evaporated to dryness at 270° F. in weighed platinum dish. Increased weight of dish represents ***total solid residue.*** (Can be used for SO_4 when sample is small.) Ignite for organic loss.

250 cc. Titrate with N/10 acid or alkali for ***alkalinity or acidity.*** (Can be re-used to make up volume of 500-cc. portion when water sample is small.) Methyl orange indicator.

100 cc. Titrate with N/10 $AgNO_3$ for ***chlorine.***

100 cc. Acidify, boil, precipitate with $BaCl_2$, filter and weigh for ***total sulphate.*** (Use filtrate for Na and K when necessary.)

100 cc. Add 2 cc. 10% Na_2CO_3, evaporate to dryness, add phenolsulphonic acid, dilute, then excess of NH_4OH for ***total nitrate.***

500 cc. Evaporate to dryness (with a few cc. concentrated HCl when very accurate SiO_2 figure is necessary) in No. 8 R. B. dish. Bake 30 minutes, cool, add boiling HCl (concentrated), dilute and filter.

<table>
<tr><td rowspan="3">Precipitate is SiO_2 and silicate impurities (also $BaSO_4$). Unless great accuracy is necessary, it should be weighed as such, otherwise SiO_2 can be removed by HFl and correction made.</td><td colspan="3">Filtrate. Add a few drops of HNO_3, concentrate to 50 cc., cool, add NH_4OH, boil and filter.</td></tr>
<tr><td rowspan="2">Precipitate (Fe,Al, Phos.) may be reported as such or as Fe and Al after Qual. test for phosphate has shown same to be absent. Otherwise both Fe and Phos should be determined and weight corrected.</td><td colspan="2">Filtrate. Boil and add saturated Am. Oxalate drop by drop, boil and filter.</td></tr>
<tr><td>Prec. Ca as oxalate, dry, ignite and weigh as $CaCO_3$ or CaO.</td><td>Filtrate Mg (and Mn) add 50 cc. concentrated Sod. Phos. Solution, then 50 cc. NH_4OH, stir well 2 minutes, or more, let stand 4 hours, or more, filter and wash with 3% NH_4OH. Ignite and weigh (determine Mn separately and correct when necessary.</td></tr>
</table>

NOTE. For industrial purposes the original addition of HCl is not always necessary and correction for $BaSO_4$ Phos. Mn and separation of Fe and Al can be dispensed with unless there is cause to suspect one to be present in material amounts.

In the matter of mineral analysis of water, it is not so hard to obtain a complete analysis of the water, including the non-incrusting or "nearly always" soluble materials as well as the incrusting materials, as it is to make numberless individual or independent tests, in the hope of drawing conclusions from same. The scheme of analysis which follows is used exclusively in the writer's laboratories, and when carried out as given, makes it possible to complete analysis of a water, or a group of waters numbering up to ten, in the period of eight hours elapsed time, or twenty-four hours, assuming the work is arranged in such a way that the magnesia precipitates are allowed to stand overnight before filtration. On another page will be found a skeleton form for this complete analysis, and this skeleton will serve as a rough guide to the more extended discussion which will follow.

The complete analysis considers the quantitative determinations of silica, iron and aluminum, calcium, magnesium, sodium and potassium, as bases, and carbonate, hydrate, nitrate, sulphate, chloride, and phosphate, as radicals or acids, with suggested methods for manganese, ammonia, barium, and other materials which might possibly be present.

Prior to the starting of the analysis, the physical characteristics of the water should be noted, turbid waters should be filtered, the suspended matter analyzed separately when necessary, and the amount determined either by filtration and weighing of the separated material (alundum cones are very satisfactory), or by the difference between two residues, one of which represents the original water and one the filtered water. The mineral analysis should represent the filtered supply. This is due to the difficulty of getting uniform samples with suspended matter at different times.

Silica, Iron, Aluminum, Calcium, Magnesium

(Manganese, Phosphoric Acid)

NOTE. If from qualitative observations the water contains considerable mineral matter, smaller quantities varying from 100 to 250 cc. may be taken, or if the sample is apparently distilled or condensed and contains very little mineral matter, 1000 cc. should be taken, the object being to obtain a residue neither too large nor too small. 0.4 to 0.6 gram is a good quantity to work on.

Silica

Evaporate over free flame, then on ¼-in. asbestos board, to dryness, 500 cc. original water, using a No. 8 porcelain dish. Bake at 110–130° C. or on asbestos plate over flame for one-half hour. Moisten with 10 cc. concentrated HCl, add 50 cc. of water, boil fifteen to thirty seconds and filter. Wash with hot water.

NOTE. For great accuracy, evaporate twice to dryness as above, with the addition, prior to the sample going to dryness, of 10 cc. HCl, allow to bake as above, following from there on the usual procedure for filtration.

The precipitate retained on the filter paper represents the silica or siliceous matter, including possibly barium sulphate. Ignite and weigh.

NOTE. If the amount is over .01 gm. per liter, or 8 parts per million, moisten with a few drops of concentrated sulphuric acid and hydrofluoric acid, expel excess acids, and reweigh. This must be done in platinum. The loss represents silica, and should

be recorded as such, and the residue represents bases, principally barium, combined with sulphuric acid. This will also catch possible calcium sulphate that might be left undissolved, due to short boiling, to low dilution, or conditions which would prevent its normal solubility in the original solution.

Iron and Aluminum (Gravimetric)

The filtrate contains iron, aluminum, calcium, magnesium, possibly manganese, and phosphate. Bring to a boil, add two or three drops conc. nitric acid and concentrate to about 25 cc. Remove from hot plate or flame, add ammonium hydroxide in slight excess, boil for one or two minutes, and filter.

The precipitate contains iron, aluminum, and possibly phosphates. Burn and weigh as oxides of iron and aluminum, plus phosphates, and test 50 cc. of the original water with treatment in the usual way to determine whether or not phosphates are present. Where this precipitate of iron and aluminum oxides is greater than 0.01 gm. per liter or 8 parts per million, or where the separation of the iron and aluminum is advisable, the precipitate should be fused with eight or ten times its weight of potassium bisulphate, redissolved in water, the iron reduced to the ferrous condition with zinc, and titrated with potassium permanganate, recording the difference in weight between the original precipitate and the iron determination as aluminum oxide.

$$Fe \times 1.43 = Fe_2O_3.$$

NOTE. Where much water is available and time is an object, an additional 500 cc. can be carried down to approximately 50 cc. with a few drops of nitric acid, the iron and aluminum precipitated as above mentioned with ammonia, and the precipitate before drying redissolved in acid, reduced and titrated with potassium permanganate. This portion can be started at the same time the original analysis is started, and will greatly simplify the determination and save time.

Total Iron (Colorimetric)

Reagents. ***Iron Standard.*** 0.7 gm. cryst. ferrous ammonium sulphate is dissolved in a small amount of distilled water, add 25 cc. dilute (1–5) sulphuric acid, warm slightly and oxidize completely with potassium permanganate, make up to 1000 cc. 1 cc. = 0.1 mg. Fe.

Potassium Sulphocyanide. 2 per cent solution.

Potassium Permanganate. 6.3 gms. per liter.

Operation. Instead of precipitating, or where *traces* of Fe are of importance, 100 cc. to 1000 cc. of the water may be carried to dryness with HCl and a few drops of Br, taken up with 5 cc. (1 : 1) HCl, diluted to 100 cc. in a Nessler tube, 10 cc. KCNS solution (20 gms. to a liter) added and the color compared with standards. The comparison should be made at once as the color fades.

NOTE. It is frequently as satisfactory to add the standard iron solution from a burette to a 100 cc. Nessler tube containing 5 cc. (1 : 1) hydrochloric acid (Fe free), 10 cc. potassium sulphocyanide solution (20 gms. to a liter) and sufficient distilled water until the color matches that of the sample.

(Ferrous Iron Colorimetric)

(Frequently desirable in acid waters but rarely necessary.)

Reagents. ***Iron Standard.*** 0.7 gm. cryst. ferrous ammonium sulphate is dissolved in one liter of distilled water containing 10 cc. dilute H_2SO_4. (Not permanent. Should be made up as needed.) 1 cc. = 0.1 mg. Fe.

Potassium Ferricyanide Solution. (Prepare as needed.) 0.5 g. per 100 cc. distilled water.

Sulphuric Acid. 1 : 5.

NOTE. Prepare sample and standards at same time.

Operation. Place in 100 cc. Nessler jar 50 cc. of sample, 10 cc. dilute H_2SO_4 (1–5), filter, if necessary, to remove suspended matter, add 15 cc. potassium ferricyanide solution and make up to 100 cc. mark with distilled water. Compare with standards made as follows:

Place in 100 cc. Nessler jar 75 cc. distilled water, 10 cc. dilute H_2SO_4 (1–5) and 15 cc. potassium ferricyanide solution, and mix well. Add various amounts of iron standard from burette, mix and compare color. Determine ferric iron by deduction of ferrous iron from total iron.

Phosphates

Reagents. ***Ammonium Molybdate.*** 50 gms. c.p. neutral salt dissolved in 1 liter distilled water.

Nitric Acid (spec. grav. 1.07). Dilute about 1–5 with distilled water.

Standard Phosphate Solution. 0.5324 gm. c.p. cryst. Na_2HPO_4, $12H_2O$. Dissolve in distilled water, 100 cc. standard HNO_3 added. Dilute to 1 liter.

One cc. = 0.0001 gram P_2O_5.

Operation. Evaporate 50 cc. water to dryness in porcelain after addition of 3 cc. HNO_3 (spec. grav. 1.07). Bake two hours at 212° F. Take up with 50 cc. distilled water, add 4 cc. molybdate solution and 2 cc. HNO_3, and compare in Nessler tube with standards from phosphate solution made to 50 cc. and treated with same reagents. A tube 2.5 cm. by 24 cm. to 100-cc. mark of hard, white glass is most suitable.[1] Where waters are already colored the evaporation should be carried on with 3 cc. HNO_3 and 0.5 cc. (or more, if water is highly colored) of $KMnO_4$ solution, (1 gram per 1000 cc.), baking at 212° F. for the same time.[2] Where the phosphate is present in large enough quantities to precipitate the gravimetric methods may be used.

Calcium

The filtrate from iron, aluminum and phosphate precipitate contains calcium, magnesium, and possibly manganese. Concentrate to about 100 cc. Add to the hot ammoniacal solution a concentrated (saturated) solution of ammonium oxalate drop by drop, or add in small portions crystals of ammonium oxalate. Allow to boil two minutes, stirring, if necessary (on account of heavy precipitate and tendency to bump), remove, filter and wash. (Five complete washings are usually sufficient.)

NOTE. Where great accuracy is desired, the precipitate on the filter should be redissolved in a small amount of hot, dilute, hydrochloric acid and reprecipitated with ammonium oxalate.

The calcium oxalate upon the filter paper can now be burned and weighed either as calcium oxide or calcium carbonate.

[1] J. Am. Chem. Soc., **23**, 96, 1901.
[2] J. Ind. and Eng. Chem., 5, 301–2, 1913.

NOTE. The burning of calcium oxalate to carbonate is not so difficult as it seems, as an intense heat is necessary to convert it to the oxide, and if the crucible is well watched and the flame gives just sufficient heat to carbonize and destroy the filter paper, there will be no chance whatever of any calcium oxide being formed, or any calcium oxalate being left. Where hypothetical combinations are used, it is very convenient to have the calcium as carbonate without calculation. Where burned to the complete oxide it is frequently necessary to use a blast lamp, as large precipitates require a high temperature to reduce completely to oxide form.

Optional (Volumetric)

Or it may be dissolved in 2% sulphuric acid and titrated with the standard solution of potassium permanganate. (N/50 $KMnO_4$ may be used.)

NOTE. Where the volumetric method is to be used, five complete washings are not, as a rule, sufficient, as the presence of traces of ammonia salts, while not interfering in any way with the gravimetric determination, are prone to have considerable influence upon the volumetric results, due to the possibility of traces of ammonium oxalate still being present.

Fe Value $\times$ 0.895 = $CaCO_3$.
Fe Value $\times$ 0.5016 = CaO.
Fe Value $\times$ 0.3584 = Ca.

Magnesium

The filtrate contains magnesium (and possibly manganese). Acidify with HCl, concentrate, if necessary, to 150 cc., add 25 cc. saturated solution of ammonium sodium hydrogenp hosphate (NH_4NaHPO_4, $4H_2O$, microcosmic salt), cool and make alkaline with ammonium hydrate. Allow to stand at least four hours, filter and wash with 3% solution of ammonium hydrate. Burn and weigh as $Mg_2P_2O_7$.

NOTE. Accurate results are also obtained with the use of sodium phosphate added direct to the filtrate from the calcium precipitate without previously acidifying with acid, with 25 cc. to 50 cc. of ammonium hydrate added to make strongly alkaline, after which the solution should be very thoroughly stirred (for at least two minutes), using a rubber-ended glass rod. Allow to stand at least four hours.

For very rapid work in either case, if the magnesium solution after the precipitation is cooled in ice-water, filtration can be frequently made in two hours' time.

For extremely accurate work the precipitate produced in either of the methods above should be redissolved in a little dilute HCl and the precipitation repeated.

Optional (Volumetric)

Reagent. ***Sodium Arsenate,*** 10% solution.

The filtrate from the calcium precipitate, or an original portion of 500 cc. from which iron, aluminum and calcium have been removed as above, is acidified. Concentrate to the point of crystallization, after which approximately one-third by volume of ammonium hydrate and 25 cc. sodium arsenate solution are added and the solution vigorously shaken for at least ten minutes, filtered, and the precipitate washed free from arsenic with distilled water to which has been added 3% C.P. ammonia water. Dissolve in 50 cc. dilute H_2SO_4 (1:3), transfer to precipitation flask, dilute to approximately 100 cc. and add 3.4 grams potassium iodide. Allow to stand five minutes and titrate with standard thiosulphate solution until the yellow color of the liberated iodine just disappears. Starch as an indicator is not satisfactory, nor necessary. This method is not so accurate as the gravimetric method, giving slightly high results, but is good for rapid work.[1]

[1] J. Am. Chem. Soc., **29**, 1464–7; ibid, **21**, 146.

Manganese

Where necessary, manganese should be determined separately in another portion of the water and corrections made. The Knorres Persulphate method is the most reliable for large amounts (10 milligrams Mn per liter); the Bismuthate method for smaller amounts.

Knorres, Persulphate Method (Volumetric)

Reagents. ***Potassium Bisulphate*** C. P.

Ammonium Persulphate Solution (60 grams per liter distilled water).

Hydrogen Peroxide Solution. Equivalent to N/10 $KMnO_4$. (Approx. 5.6 cc., 3% H_2O_2 diluted to 100 cc.)

Operation. Evaporate 5 liters or more to dryness, adding first 10 cc. concentrated H_2SO_4. Ignite after adding a few crystals of potassium bisulphate and take up in hot water. Transfer to 250-cc. Erlenmeyer flask with 5 cc. dilute (1 : 3) H_2SO_4, add 10 cc. ammonium persulphate solution, boil twenty minutes, cool, dissolve precipitate (manganese superoxide) in standard hydrogen peroxide solution. (If no ppt. forms no manganese is present.)

NOTES. When hydrogen peroxide solution is standardized against N/10 $KMnO_4$ 1 cc. will be equivalent to 2.754 milligram Mn.

An excess of 10–20 cc. H_2O_2 Sol. can be added and this excess titrated with N/10 $KMnO_4$.

Sodium Bismuthate Method (Colorimetric)[1]

Reagents. ***Potassium Permanganate.*** 0.288 gram $KMnO_4$ to 1000 cc. 1 cc. = 0.1 milligram Mn.

Sodium Bismuthate (purest).

NOTE. Bismuth subnitrate may be substituted.

Nitric Acid. (Spec. grav. 1.135) 3 parts concentrated HNO_3 to 1 part H_2O should be blown with air until free from oxides of nitrogen.

Sulphuric Acid. 25 cc. concentrated H_2SO_4 to 1000 cc. Add permanganate solution to a faint but noticeable color.

Operation. Evaporate 500 cc. in porcelain dish after adding 1 cc. dilute H_2SO_4 in excess to that necessary to neutralize all alkali. Ignite to remove free acid (organic matter and chlorine), cool and dissolve in 50 cc. HNO_3 (30 cc. concentrated HNO_3 to 1 liter), with heat if necessary. Cool again, add 0.5 gram sodium bismuthate and heat until pink color disappears, re-cool and add sodium bismuthate in excess, filter through asbestos in Gooch crucible (asbestos must be free from organic matter, thoroughly washed and ignited), or alundum crucible. Wash with nitrite-free distilled water containing 5% dilute HNO_3 (30 cc. concentrated HNO_3 per liter), into Nessler tube, make up to 100 cc. and match with color produced by necessary amount of standard $KMnO_4$ in 100 cc. H_2SO_4 reagent.

No. cc. standard $KMnO_4 \times 0.2$ = milligrams Mn per liter.

NOTE. The permanganate solution used for oxygen consumed (see Sanitary Method) contains 0.139 gram Mn per liter and may be used when necessary.

No. cc. $\times$ 0.278 = milligram Mn per liter.

[1] J. Am. Chem. Soc., **29**, 1074–78, 1907.

Sulphates

100 cc. of the water is slightly acidified with conc. HCl and 5 cc. 10 % NH_4Cl solution added, brought to a boil, and if turbid is filtered and washed four or five times with boiling water. The clear or original water is now brought to a boil and 10% barium chloride added drop by drop to the boiling solution in slight excess. Boil ten minutes, stirring from time to time, if the precipitate is heavy. Remove and *allow to cool* prior to filtering. The precipitate consists of barium sulphate. Wash free from chlorides, testing with $AgNO_3$. Dry, ignite and weigh.

$$BaSO_4 \times .411 = SO_4.$$
$$BaSO_4 \times .583 = CaSO_4.$$
$$\text{milligrams } BaSO_4 \times .338 = CaSO_4 \text{ grains per gallon.}$$

Benzidine Method (Optional)[1]

Reagents. ***Benzidine Solution.*** Triturate in a mortar with 5 cc. to 10 cc. water, 4 grams benzidine base. Transfer to liter flask, add 10 cc. HCl and make to volume. 1 cc. = .0013 gram SO_4.

Hydroxylamine Hydrochloride. 1% solution in water.

Operation. Add 10 cc. hydroxylamine hydrochloride to 250 cc. water, then add, at once stirring well, 100 cc. benzidine solution. Allow to stand fifteen to twenty minutes, decant through vacuum filter and wash with 10 cc. to 20 cc. distilled water (do not let filter run dry), return filter paper to beaker, cover with distilled water, bring to a boil and titrate with N/10 or N/50 NaOH, using phenolphthalein as indicator.

$$\text{One cc. N/10 NaOH} = .0048 \text{ gram } SO_4.$$
$$\text{One cc. N/50 NaOH} = .00096 \text{ gram } SO_4.$$

NOTE. An accurate method by the turbidimeter is given by Hale in the chapter on Coal, page 675.

N. B. Method by Muer, Jour. Ind. Eng. Chem., Vol. 3, Aug., 1911. When the sulphate is 25 p.p.m. or more, the determination may be made by the turbidimeter method direct on 100 cc. For less quantities, larger amounts of water are taken and evaporated.

Sodium and Potassium

The filtrate contains sodium and potassium and may be used for such unless the water is highly mineralized, in which case *a new portion, 100 cc. to 500 cc., should be taken.*

Evaporate to dryness, add saturated solution of barium hydrate in excess, filter, wash with hot water, add to the filtrate ammonium carbonate in excess and a few drops of ammonium oxalate, boil, filter, evaporate again to dryness and dry at a high temperature to expel excess of ammonia salts. Redissolve, add slight excess of ammonium carbonate again and continue until no further precipitate is formed on such addition. Evaporate to dryness in a weighed platinum dish, remove ammonium salts by high-temperature drying, and weigh the combined chlorides of sodium and potassium. Moisten with about 25 cc. of water and a few drops of HCl and add from 1 cc. to 5 cc. of 10% solution of platinic chloride

[1] Freidbaum and Nydegger, Z. Agnew. Chem., 1907-9.

(1 cc. to each 25 milligrams to 30 milligrams total chlorides). Evaporate to dryness on water bath, take up and wash with 95% alcohol until filtrate is free from color. Dry, redissolve precipitate, washing through the filter paper in hot water. Evaporate again to dryness and weigh as K_2PtCl_6.

$$K_2PtCl_6 \times .161 = K.$$
$$K_2PtCl_6 \times .307 = KCl.$$

Deduct from combined weight of chlorides. Remaining $NaCl \times .394 = Na$.

NOTE. When separation is not necessary, the combined chlorides are calculated as sodium chloride and reported as sodium and potassium chlorides.

Alkalinity

In ordinary cases titrate with N/10 or N/50 H_2SO_4, using methyl orange as indicator. Special cases will be considered later.

Reagents. Sulphuric acid, N/10. Methyl orange. Phenolphthalein.

Operation. 250 cc. of water in 400-cc. beaker or a casserole are titrated with N/10 H_2SO_4, using two to five drops of methyl orange indicator (or 50 cc. can be similarly titrated with N/50 H_2SO_4).

Calculate for 250-cc. sample.

$$\text{No. cc.} \times 4 \times .005 = \text{gms. per liter } CaCO_3.$$
$$\text{No. cc.} \times 4 \times 58.4 \times .005 = \text{grs. per gallon } CaCO_3.$$
$$\text{Or} \quad \times 1.168 = \text{grs. per gallon } CaCO_3.$$

Distilled water, and neutral waters containing magnesium chloride and magnesium sulphate frequently give an alkaline reaction when used with methyl orange. In such cases from .2 to .8 cc. N/10 acid are required to discharge the alkaline color of the methyl orange. Such a procedure would suggest to the operator that the waters were alkaline. However, if such neutral waters are boiled with phenolphthalein as an indicator for twenty minutes and no pink color develops, the waters are not alkaline but neutral. The use of a blank of .2 cc. is of no value under such conditions and it appears to the writer as much the safest way when the titration is under 1 cc. of N/10 acid that the water be boiled with phenolphthalein in an effort to determine absolutely whether this water is alkaline, due to the presence of a carbonate as indicated by the methyl orange, or whether the alkalinity is entirely due to the hydrolyzing of the calcium or magnesium base present in the absence of alkali. When no pink color is produced the water should be pronounced neutral.

Phenolphthalein may also be used as indicator on another 250-cc. portion, using the above procedure. This titration in connection with the methyl orange titration makes possible a determination of the relation of carbonate, bicarbonate and caustic alkalinity.

The following is adapted from a table on page 39, Standard Methods of Water Analysis of the American Public Health Association, and is of value in showing the relation of the various titrations. Methyl orange has been used in place of erythrosine.

'ABLE SHOWING RELATION BETWEEN ALKALINITY BY PHENOLPHTHALEIN AND THAT BY METHYL ORANGE IN PRESENCE OF BICARBONATES, CARBONATES AND HYDRATES.

	Bicarbonates.	Carbonates.	Hydrates.
'=O	M	O	O
'<½M	M–2P	2P	O
'=½M	O	2P	O
'>½M	O	2(M–P)	2P–M
'=M	O	O	M

M = Methyl orange alkalinity.
P = Phenolphthalein alkalinity.

Acidity

For acidity use N/10 Na_2CO_3 and 250 cc. water.

Acidity due to	Indicator.	Hot or Cold.
'arbonic and sulphuric acids, also Fe and Al sulphates	Phenolphthalein	Cold
ulphuric acid, also Fe and Al sulphates	Phenolphthalein	Boiling
ulphuric acid alone. When desired, 20 cc. N/10 H_2SO_4 may be added. Boil fifteen to twenty minutes, cool and titrate, noting the excess of acidity over the original 20 cc.	Methyl orange	Cold

Free Carbonic Acid [1]

Reagents. Either standard N/10 sodium carbonate or standard N/22 sodium arbonate. For the latter dissolve 2.41 grams of dry sodium carbonate in one liter f distilled water which has been boiled and cooled in a carbon dioxide free tmosphere. Hold both solutions in glass bottles protected by tubes filled with oda-lime.

One cc. N/10 Na_2CO_3 = 2.2 milligrams CO_2.
One cc. N/22 Na_2CO_3 = 1.0 milligram CO_2.

Operation. With N/10 sodium carbonate titrate 250 cc. of sample in 400-c. beaker, using phenolphthalein as indicator. First faint but permanent pink lenotes end-point.

Using 250 cc.

No. cc. N/10 $Na_2CO_3 \times 8.8 = CO_2$ parts per million.
No. cc. N/10 $Na_2CO_3 \times .513 = CO_2$ grains per gallon.

With N/22 sodium carbonate solution, use 100 cc. of sample, preferably n 100-cc. Nessler tube, titrate and rotate the tube until faint but permanent

[1] For criticisms of this method see Z. Nahr. Genussm., **24**, 429, also Chem. Abs., 5, 1024; C.A., **6**, 3137; C.A., **7**, 38.

pink color 30 seconds without fading is produced, using phenolphthalein as indicator

Using 100 cc.

No. cc. N/2 $Na_2CO_3 \times 10 = CO_2$ parts per million.
No. cc. N/2 $Na_2CO_3 \times .583 = CO_2$ grains per gallon.

Chlorine

Titrate 100 cc. of water, using 1 cc. of 10% potassium chromate as an indicator, with N/10 $AgNO_3$ to first permanent indication of the red silver chromate. (Acid waters should be neutralized and sulphide waters boiled with a drop or so of nitric acid and then neutralized for reliable results.)

No. cc. $\times 3.42$ = grs. per gallon NaCl.
No. cc. $\times 58.46$ = parts per million NaCl.
No. cc. $\times 35.46$ = parts per million Cl.

NOTE. Where qualitative test shows chlorine to be high, smaller portions of the sample should be taken, either by certified pipette, or burette, and when the titration with N/10 $AgNO_3$ is less than .2 cc., N/50 or N/100 $AgNO_3$ should be used for accuracy.

Nitrates

(Also see Sanitary Analysis)

Evaporate 100 cc. of water, after adding 2 cc. 10% Na_2CO_3, to dryness, cool, moisten with 2 cc. phenolsulphonic acid, add 50 cc. water and then NH_4OH until slightly ammoniacal. Yellow coloration shows presence of nitrates. Compare with standards which should be renewed every month, or oftener. Less than $\frac{1}{8}$ grain per gallon, or about 2 parts per million as KNO_3, while of value in sanitary analyses, usually rank as "trace" in mineral waters.

Where nitrates are high, 85 to 90 parts per million, or 5 grains per gallon and over, colorimetric methods do not always give reliable results, and 500 cc. of the water should be first boiled with a slight excess of acid, then made alkaline with sodium or potassium hydroxide, reduced with 10 grams each of powdered Zn and Fe, or 10 grams powdered Al, and distilled into an excess of N/10 or N/100 HCl, as the case may be, and titrated back, using cochineal as indicator, and calculating the ammonia absorbed to NO_3 or $Ca(NO_3)_2$ as desired. (Where free ammonia or its compounds are present corrections must be made.)

A recent modification of this method depends upon the absorption of ammonia into a solution of boric acid (5 grams boric acid in 100 cc. of water). Due to the very weak acidity of the boric acid, it is possible to titrate the ammonia direct with standard acid, using methyl orange as an indicator, and this has the advantage of doing away with two standard solutions. The boric acid strength is based upon 5 grams of boric acid to 100 cc. of water to each .2 gram of ammonia absorbed. It is stated that even the cooled condenser is unnecessary, in this absorption.[1]

[1] The Volumetric Determination of Ammonia. L. W. Winkler, Budapest. Z. angew. Chem., **26**, Aufsatzteil, 231–2.

Determination of Ammonia by the Boric Acid Method. L. W. Winkler, Z. angew. Chem., **27**, I, 630–2, 1914.

The Determination of Ammonia by the Boric Acid Method. E. Bernard, Z. angew. Chem., **27**, I, 664, 1914.

Ammonia and Its Compounds

Place 500 cc. or less in an 800-cc. Kjeldahl flask, make alkaline and distill nto N/10, or weaker, HCl, titrate with cochineal or Nesslerize. (See Sanitary nalysis, page 536.)

Total Mineral Residue

Use a clean weighed platinum dish. Evaporate 50 cc. (certified pipette) to lryness at about 130° C. and bake for at least thirty minutes at that temperature.)rdinary water-bath temperature will not remove water of crystallization from Na_2SO_4 or $CaSO_4$. Weigh to the fourth decimal or .0001 gram.

Weight × 1168 = grains per gallon.

0.1 milligram = 2 parts per million.

Residues of acid waters should be ignited to a dull red heat. Where the acidity is low a drop or so of sulphuric acid should be added to assure the fixation of all sodium and potassium salts as the sulphate. The ignition should be complete so that no free acid is left behind and to assure the decomposition of all iron compounds to the oxide form. In calculating, correction must be made for the change in the iron salts and all other compounds converted to the sulphate form for comparison with the sulphated residue, and then the proper corrections made to give the theoretical residue on the original water.

Waters with much organic matter, after weighing, may be gently ignited until the carbon has been burned off, cooled, recarbonated with tested $(NH_4)_2CO_3$ dried and again weighed. The difference in weight after titrating for possible volatilized chlorides gives approximately the organic matter present.

Waters high in easily decomposed $MgCl_2$ or $(CaNO_3)_2$ should be evaporated with a few drops excess of H_2SO_4, or Na_2CO_3, and the residue compared with an addition of all bases calculated to the sulphate form, or corrected for added carbonate.

NOTE. When acid is used, ignite to a dull red heat; when carbonate, evaporate as in the case of the original residue.

Hydrogen Sulphide

Due to the fact that hydrogen sulphide is frequently very transient and often oxidizes to sulphate in transit, it is advisable to collect this sample in a special container at the point of sampling. Two or three bottles holding exactly 250 cc. of water each, are used, each bottle containing 50 cc. N/100 iodine solution. The water placed in the bottle is sealed. The sample is titrated with standard N/100 sodium thiosulphate upon receipt at laboratory, at which time a blank is run, using 50 cc. iodine solution made to mark with distilled water. The difference between the titration of the sample and the blank represents hydrogen sulphide present.

Iodine value × 0.1263 × 4 = sulphur value grams per liter.

Oil

Frequently waters from condensing engine, or after passing heaters or oil separators, still contain oil in small quantities. The following method has been found most satisfactory:

Reagents. ***Ferric Chloride Solution.*** (10 grams of iron dissolved in 200 cc. HCl, oxidized with HNO_3 and made to one liter.)

Ammonia C.P.

NOTE. If the oil exceeds 0.4 grain per gallon, use 500 cc., or less for the determination; if below 0.4 grain per gallon use 1 liter.

Operation. Add to the water taken in a large beaker or flask 5 cc. of the "ferric chloride" solution and heat nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

Allow to stand a few minutes and filter through a 15 cm. filter paper which has been previously extracted with ether, transferring the precipitate on to the paper with hot water, and washing three or four times with hot water. Then dry both filter and precipitate in the water oven at 100° C. and when dry, extract with ether in the soxhlet in the usual way, evaporate the ether extract and weigh the remaining oil.

Dissolved Oxygen

Use the Winkler Method[1]

Reagents. No. 1. ***Manganous Sulphate Solution.*** 48 grams manganous sulphate dissolved in 100 cc. distilled water.

No. 2. ***Iodide Solution.*** 360 grams NaOH and 100 grams KI dissolved in 1 liter of distilled water.

No. 3. ***Concentrated hydrochloric acid, or sulphuric acid sp.gr. 1.4 (dilute 1 : 1).***

No. 4. ***Sodium Thiosulphate Solution.*** N/100 solution is made as needed from the N/10 stock solution.

NOTE. Not permanent; should be frequently restandardized against N/100 potassium bichromate.

The addition of 5 cc. of chloroform plus 1.5 grams sodium or ammonium carbonate to each liter of solution on mixing will improve its keeping quality.

N/40 sodium thiosulphate containing 6.2 grams C.P. recrystallized salt per liter may be preferred to N/100 strength. 1 cc. of this solution is equivalent to 0.2 milligram oxygen by weight or 0.1395 cc. oxygen by volume, standard conditions.

5. ***Starch Solution.***[2] The starch should first be made into a thin paste with cold water and about 200 times its weight of boiling water stirred in and boiled for a few minutes. A few drops of chloroform will assist in preserving this solution.

Collection of Sample. A small-necked, 250-cc. bottle should be used, etched or otherwise marked, with its exact volume previously determined. The collec-

[1] Ber. deutsche Chem. Gesell., **21**, 2843, 1888. Also Z. Anal. Chem., **53**, 665-72, 1914; C.F.C.A., 8, 674, 1915.

[2] Hale gives the following method. "Rub 5 grams of potato starch with cold water to a thin paste together with 10 milligrams of mercuric iodide. Pour into one liter of boiling water and boil half an hour."

tion should be so arranged to exclude outside air and result in several continuous changes of the contents before stoppering, care being taken to exclude air bubbles.

Operation. To sample as received add, in both cases by pipette, delivering below surface of water and away from the air, 2 cc. solution No. 1 (manganese sulphate) and No. 2 (NaOH,KI). Restopper and shake thoroughly. After precipitate has settled add 2 cc. HCl or H_2SO_4 and again mix by thorough shaking until precipitate has completely dissolved, transfer 100 cc. to flask, and titrate with solution No. 4 (sodium thiosulphate), using starch as indicator near end as the color approaches a faint yellow.

N = cc. N/100 thiosulphate solution.
V = capacity of bottle less 4 cc. (vol. sol. 1 and 2 added).
O = the amount of oxygen in parts per million in water saturated at the same temperature and pressure.

(1) Oxygen in p.p.m. $= \frac{.0008N \times 1{,}000{,}000}{100} = .8N.$[1]

(2) Oxygen in cc. per liter = .7 oxygen p.p.m.

(3) Oxygen per cent saturation $= \frac{\text{Oxygen p.p.m. (observed temp. and pres.)}}{\text{Saturation oxygen p.p.m. (observed temp. and pres.)}}$.

METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD, ZINC, COPPER AND TIN

Very frequently a determination is desired of materials which are apt to be present in water due to the solvent action of such water upon pipes and containers. In most cases the estimates are made by colorimetric methods if the amounts present are exceedingly small. As these determinations are made only in rare cases it seems advisable to summarize, calling attention to the fact that all methods may be found in full in any of the editions of Standard Methods for Water Analysis gotten out by the American Public Health Association.

Where any or all of the metals, lead, zinc, copper and iron are apt to be present, a large quantity (1 to 4 liters), of the water is evaporated. The metals are separated as sulphides with ammonia and hydrogen sulphide. The precipitate after washing is dissolved in nitric acid and refiltered to remove suspended matter and then concentrated with H_2SO_4.

The lead is removed by taking up the concentrated solution with 50% alcohol (100 cc. to 150 cc.), filtering and dissolving the precipitate in ammonium acetate, after which the solution is made to volume and divided. One-half is saturated with hydrogen sulphide water to get an approximate idea of the amount of lead present. To the other half add two to three drops of acetic acid, then an excess of hydrogen sulphide water and compare the color with standards. This gives *lead.*

The alcohol is removed from the filtrate by evaporation and it is then treated with ammonia to remove possible iron. The filtrate from the iron precipitate

[1] Correcting for displacement for 300-cc. bottle, .8N = .811N; for 275-cc. bottle, .8N = .812N.
No correction for displacement affects result .1 p.p.m. oxygen.
Twenty-five cc. variation in capacity of bottle affects result .01 p.p.m. oxygen.
The above formulæ are based upon N/100 thiosulphate, and titrating 100 cc. volume. N = cubic centimeters thiosulphate used.

is neutralized with H_2SO_4, then 2 cc. concentrated H_2SO_4 and 1 gram urea added. Copper is removed by electrolyzing (two hours with 0.5 ampere current). If the deposit is material it may be weighed as copper after washing with alcohol and drying. When the deposit is extremely small it should be dissolved in nitric acid, evaporated to dryness to remove acid taken up in water, after which potassium sulphide solution is added and the color compared with standards. This gives ***copper.***

The solution from the above is nearly neutralized with ammonia. It is then concentrated and 2 grams potassium oxalate and 1.5 grams potassium sulphate are added and the zinc removed by electrolyzing. (Three hours with 0.3 ampere current.) This gives ***zinc.***

Where copper only is desired it is frequently sufficiently satisfactory to concentrate the water from 50 cc. to 75 cc., after which it is acidified with 2 to 5 cc. concentrated H_2SO_4, depending upon whether the water is very alkaline with carbonate of lime, etc., and then the procedure for copper is followed.[1]

There is no satisfactory method for the quantitative determination of small quantities of tin. In the above-mentioned procedure, however, in case tin should be present it would be removed with the ammonia precipitate for the removal of iron and its presence may be avoided by dissolving the sulphides in the original precipitation in HNO_3, in which the tin would remain behind insoluble.

HARDNESS

Total Hardness

The most accurate method for total hardness is by calculation of the calcium and magnesium determined gravimetrically as previously outlined, calculating the calcium as calcium carbonate and the magnesium to its calcium carbonate equivalent in terms of parts per million.[2] However, where only the hardness is desired, gravimetric methods are cumbersome and the following are accepted as standard.

The standard method for the determination of total hardness, as well as temporary and permanent, depends upon the action of the lime and magnesia in solution upon soap, the soap added in a very dilute solution in alcohol. Total hardness represents the total soap acted upon by the water in its original state, permanent hardness represents the total soap acted upon by the water after the water in question has been thoroughly boiled and separated from the suspended matter, and temporary hardness represents the difference between the total hardness and the permanent hardness, and while it is supposed to represent combined carbonates of lime and magnesia, and the permanent hardness is supposed to represent lime and magnesia in other forms than carbonate, this is rarely so due to the fact that a certain material amount of carbonate of lime and magnesia is soluble in water, even in the absence of carbon dioxide gas. The reagents used are ***standard soap solution*** and ***standard calcium chloride solution,*** the latter being made under such conditions that 1 cc. of the solution is equivalent to 0.2 milligram of calcium carbonate.

[1] Phelps, Jour. Amer. Chem. Soc., **28**, 369, 1906.
[2] C. Bahlmann, J. Ind. Eng. Chem., **6**, 209, 11.

Preparation of Solutions

0.2 gram pure calcium carbonate is dissolved in a small amount of dilute HCl, taking pains to avoid any loss due to effervescence or spattering. Evaporate the solution to dryness several times to remove excess acid. Dissolve in distilled water and make up to 1 liter.

Standard soap solution is obtained by dissolving approximately 100 grams dry castile soap in 1 liter 80% alcohol. This solution should stand several days. For standardizing, this solution should be diluted with alcohol (70% to 80%), until 6.4 cc. when added to 20 cc. of standard calcium solution will produce a permanent lather. Usually less than 100 cc. of the original soap solution will make 1 liter of standard solution.

For standardizing, use 250-cc. glass-stoppered bottle, add 20 cc. calcium solution with 30 cc. distilled water. The soap solution should be added from a burette, approximately .2 cc. at a time, after which the bottle is shaken vigorously until the lather formed remains unbroken for five minutes after shaking and after the bottle has been placed upon its side.

NOTE. Pure potassium oleate and potassium carbonate may be used in place of soap.[1]

Operation. Fifty cc. of the water in question are measured into a 250-cc. bottle, the soap solution added, approximately .2 cc. at a time, and in the same manner as described for the standardizing of said soap solution. The following table, copied from p. 33, Standard Methods of Water Analysis, A.P.H.A., 1913, may be used to obtain the total hardness from the results so noted:

TABLE OF HARDNESS SHOWING THE PARTS PER MILLION OF CALCIUM CARBONATE ($CaCO_3$) FOR EACH TENTH OF A CUBIC CENTIMETER OF SOAP SOLUTION WHEN 50 CC. OF THE SAMPLE ARE USED.

cc. of Soap Solution.	0.0 cc.	0.1 cc.	0.2 cc.	0.3 cc.	0.4 cc.	0.5 cc.	0.6 cc.	0.7 cc.	0.8 cc.	0.9 cc.
0.0	....	....	....	....	....	....	....	0.0	0.6	3.2
1.0	4.8	6.3	7.9	9.5	11.1	12.7	14.3	15.6	16.9	18.2
2.0	19.5	20.8	22.1	23.4	24.7	26.0	27.3	28.6	29.9	31.2
3.0	32.5	33.8	35.1	36.4	37.7	38.0	40.3	41.6	42.9	44.3
4.0	45.7	47.1	48.6	50.0	51.4	52.9	54.3	55.7	57.1	58.6
5.0	60.0	61.4	62.9	64.3	65.7	67.1	68.6	70.0	71.4	72.9
6.0	74.3	75.7	77.1	78.6	80.0	81.4	82.9	84.3	85.7	87.1
7.0	88.6	90.0	91.4	92.9	94.3	95.7	97.1	98.6	100.0	101.5

It is not desirable to use more than 7 cc. of soap solution for 50 cc. of the water, and when the figures are higher, the water should be diluted with distilled water. The reading in the table corresponding to the cc. of soap solution

[1] C. Blacher, Chem. Ztg., **36**, 541; J. Soc. Chem. Ind., **31**, 555, C. A., **7**, 1394; C. Blacher, P. Gruenberg, M. Kissa, Chem. Ztg., **37**, 56–8, C. A., **7**, 1938. L. W. Winkler, Z. Anal. Chem., **53**, 409–15, C. A., **8**, 2912.

used is then multiplied by the quotient $\frac{50 \text{ cc.}}{x \text{ cc.}}$; x cc. being equal to the amount of water taken. In making this determination there is frequently noted a false end-point sometimes known as the magnesium end-point. To avoid error, it is advisable, after completing the titration, to read the burette, add 0.5 cc. more of the soap solution and shake well. If magnesium has been responsible for the false end-point, after such addition the lather will again disappear, and titration should be continued until a new and true end-point is reached. It is advisable to determine the strength of the soap solution from time to time, as it is very prone to change upon standing. Results should be recorded in terms of calcium carbonate, parts per million. There are various other means of reporting. The English degree frequently noted as Clark degree, represents grams calcium carbonate per Imperial gallon and should be multiplied by 14.3 to give parts per million. Conversely, the result obtained in parts per million divided by 14.3 will give Clark, or English degrees. French degrees represent parts per 100,000 calcium carbonate and should be multiplied by 10 to give parts per million. Conversely, division of the result obtained above by 10 will give French degrees. German degrees represent parts per 100,000 calcium oxide and should be multiplied by 17.8 to give parts per million calcium carbonate. The determination of hardness is not reliable on account of the varying action of calcium and magnesium salts, and should never be resorted to when possible to determine these bases direct.

NOTE. Dr. Hale claims that the soap method for hardness in skilled hands is accurate from 10 to 15 parts per million on waters as hard as 300 parts.

For *permanent hardness* the standard soap solution is used as above stated. The water, however, is boiled gently for one-half hour, allowed to cool, made to volume with boiled and cooled distilled water and filtered, after which the above method is used. The difference between total hardness and permanent hardness is supposed to represent temporary hardness. The *alkalinity* determination given on a previous page is a much more accurate method of determining temporary hardness, however, and is also much more easily carried out. When total hardness and alkalinity are determined, permanent hardness would be the difference between these two figures. For comparative use as against ***total*** and ***permanent*** hardness determined as such, the results would be much different, as the alkalinity determination of all the carbonates would give a permanent hardness representing absolutely non-carbonate hardness; whereas the determined permanent hardness would contain a material amount of combined carbonates of lime and magnesia. The American Public Health Association, Committee on Standard Method of Water Analysis, recommend that the determination of permanent hardness by the soap solution be discontinued in connection with softening process, as it is so unsatisfactory in general practice.

Magnesium Chloride

Frequently, when hypothetical combinations are used it is desired to check up these calculated combinations by some chemical method. Magnesium chloride is frequently produced in the course of hypothetical combinations and its presence is as frequently a source of much trouble in the determination of a mineral residue, owing to the ease with which it decomposes or carbonates. A method is suggested

whereby a second 50 cc. portion similar to the total mineral residue is exactly neutralized with sufficient H_2SO_4, the amount to use being calculated from the total alkalinity obtained elsewhere. The solution is allowed to go to complete dryness, is baked at a temperature of 280° F. to 300° F., and after being cooled the chlorine is titrated. The difference between the chlorine thus determined and the total chlorine previously determined represents chlorine lost by volatilization as magnesium chloride. In the absence of organic matter this method is approximately accurate. Where organic matter or other reducing material is present, however, the results are not so satisfactory.

Calcium Sulphate

In a similar manner it is frequently desired to know whether or not a water would contain calcium sulphate, and a method of comparative satisfaction depends upon the evaporation of 250 cc. to 500 cc. of the original water to dryness. After cooling, 10 cc. of distilled water are added and the mineral matter loosened from the sides of the dish and partially dissolved. Ten cc. of 95% alcohol are then added and 100 cc. of 50% alcohol. After thorough stirring and solution this material is filtered, the precipitate washed with 50% alcohol and the filtrate made to volume, divided and tested for calcium and sulphates in the usual manner. The method is only approximate.

LIME AND SODA VALUE[1]

Two very simple methods have been devised for the rapid estimation of the amount of lime and soda-ash necessary for softening, when water treatment is considered from the outside softening-plant point of view.

Value for Lime

Reagents. *Saturated lime water* (strength to be known for each series of determinations). *N/10 hydrochloric acid.*

Process. Take 200 cc. of the water in question; add 50 cc. saturated lime-water solution in 250-cc. volumetric flask and heat to boiling. Allow to cool. Fill to the 250-cc. mark with water to replace that lost by evaporation; filter through a dry-folded filter and titrate 200 cc. of the filtrate with N/10 acid, using methyl orange as an indicator.

For calculation, let " a " equal number of cc. N/10 calcium oxide in 50 cc. the lime water, as determined: and let " b " equal the number cc. N/10 hydrochloric acid used in determination.

$(4a - 5b) \times 3.51$ CaO will give milligrams of lime per liter required to soften the water tested.

Value for Soda

To the neutralized 200 cc. from above titration, add 20 cc. N/10 sodium carbonate. Heat to boiling. Transfer with CO_2 free distilled water into a 250-cc. flask to make up to mark with washings from the dish; mix thoroughly and filter, collecting 200 cc. of the filtrate in a beaker. Titrate with N/10 hydro-

[1] Drawe, Zeit. f. Angew. Chem., **23**, 52, 1910.

chloric acid for the excess alkali. Designate the number of cc. in this titration by "c."

Formula: $(20-b-\frac{1}{4}c)\times 33.13$ Na_2CO_3 = milligrams of soda per liter necessary to soften water in question.

NOTE. Both formulæ are based upon C. P. chemicals, and corrections must be made for the value of the commercial materials in use. These methods are valuable, though for actual practice it is advisable to try out on a liter of water in question, using the calculated amounts of lime and soda for experimental purposes.

METHODS OF REPORTING AND INTERPRETATION

The manner of reporting the results of a mineral analysis of any water calls for as much thought and uniformity as the methods of analysis themselves, and in this department there is much less uniformity than in the case of analytical methods. Undoubtedly, the ideal method of reporting is that which gives results in Ionic form (positive and negative radicals), in terms of parts per million or grains per gallon. The latter term is purely American and would have to be converted for comparison with results obtained in almost any foreign country. Parts per million, though newer and still unfamiliar to all but professional and scientific men, is gaining gradually a strong foothold, and the consideration of this terminology with the Ionic form of reporting will be considered prior to the discussion of hypothetical combination and grains per gallon.

Mr. Herman Stabler,[1] and R. B. Dole,[2] of the United States Geological Survey, have devised and simplified certain calculations and formulas, which greatly assist in the interpretation, comparison, and classification of waters for Industrial and Irrigation[3] purposes. Formulas with reference to dissolved solids will be the only ones discussed here. The following table gives reaction coefficients:

Positive Radicals.	Reaction Coefficients.	Negative Radicals.	Reaction Coefficients
Ferrous Iron (Fe)	0.0358	Carbonate (CO_3)	0.0333
Aluminum (Al)	.1107	Bicarbonate (HCO_3)	.0164
Calcium (Ca)	.0499	Sulphate (SO_4)	.0208
Magnesium (Mg)	.0822	Chlorine (Cl)	.0282
Sodium (Na)	.0435	Nitrate (NO_3)	.0161
Potassium (K)	.0256		
Hydrogen (H)	.992		

Using the above table, the parts per million of each radical multiplied by its reacting coefficient will give its reacting value, and in the formulas which follow this will be indicated by "r" prefixed to the chemical symbol of the radical.

For checking the accuracy of the analysis, the sum of the positive reacting values should equal the sum of the negative reacting values, and the formula $100\,\frac{\text{r. Pos.} - \text{r Neg.}}{\text{r. Pos.} + \text{r Neg.}} = \text{E}$, the percentage error of the analysis. The value of this error should never exceed 5 for waters of 100 p.p.m. or more dissolved solids, and should be 2 or less.

[1] Eng. News, 60, 355, 1909.
[2] Water Supply Paper No. 274, p. 165, Water Supply Paper No. 254, J. Ind. and Eng. Chem., 6, (1914), No. 7, p. 710.
[3] U. S. G. S. W. S. Paper, 274, p. 177.

In ordinary analysis, silica, iron and aluminum are present in such small quantities that they may, for simplicity's sake, be ignored. The following formulas are given without comment, as full details can be found in Water Supply Paper No. 274.

Water Softening

For 1000 Gals. Water. Pounds lime (90% CaO) required
$$=0.26(rFe+rAl+rMg+rH+rHCO_3+.0454\,CO_2).$$

Pounds soda ash (95% Na_2CO_3) required
$$=0.465(rFe+rAl+rCa+rMg+rH-rCO_3-rHCO_3).$$

NOTE. Dr. Hale states the following. Instead of the extended formulæ of the Ionic system, I much prefer my simple formulæ.

(Alkalinity $\times .44$ + free CO_2) $\times .0106$ = lbs. CaO per 1000 gals. feed water.

Also (Total hardness − total lime) $\times .0047$ = lbs. CaO per 1000 gals. feed water. or total magnesia as $CaCO_3$.

(Total hardness − alkalinity) $\times .009$ = lbs. Na_2CO_3 per 1000 gals. feed water. Expressed as $CaCO_3$.

Foaming and Priming

Foaming coefficient F = 2.7 Na.

Taking into consideration the various boilers and the action of various waters in practice, the following approximate classification of waters for foaming conditions is of value:

Non-foaming, F = 60 or less.
Semi-foaming, F = 60–200.
Foaming, F = 200 or more.

Corrosion

For Acid Waters

Coefficient of corrosion $C = 1.008(rH+rAl+rFe+rMg-rCO_3-rHCO_3)$.

For Alkaline Waters

$$C = rMg - rHCO_3.$$

If C is positive, water will corrode.

If C + .0503 Ca is negative, water will not corrode on account of the mineral materials in the water.

If C is negative, but C − .0503 Ca is positive, the water may or may not corrode.

Scale

$$SiO_2+2.95\ Ca+1.66\ Mg = \text{scale p.p.m.},$$

or

[1] (.00833 Sm + .00833 Cm + .3 rFe + .142 rAl) + .168 rMg + .492 rCa
= scale lbs. per 1000 gallons.

[1] Can be omitted or ignored unless suspended matter, silica, etc., are present in large quantities.

There are also formulas given in the above-mentioned Bulletin on soap cost, lime, soda, soda ash, cost hard scale (pounds per 1000 gallons) and a hardness coefficient of the scale formation.

Irrigating Waters

Alkali Coefficient

(*a*) When Na − .65 Cl is zero or negative.

$$\text{Alkali coefficient, } k = \frac{2040}{Cl}.$$

(*b*) When Na − .65 Cl is positive, but not greater than .48 SO_4,

$$\text{Alkali coefficient, } k = \frac{6620}{Na + 2.6\ Cl}.$$

(*c*) When Na − .65 Cl − .48 SO_4 is positive,

$$\text{Alkali coefficient, } k = \frac{662}{Na - .32\ Cl - .43\ SO_4}.$$

Classification on basis of alkali coefficient:

Alkali cpefficient.	Class.	Remarks.
More than 18...	Good...	Have been used successfully for many years without special care to prevent alkali accumulation.
18 to 6.....	Fair....	Special care to prevent gradual alkali accumulation has generally been found necessary except on loose soils with free drainage.
5.9 to 1.2.....	Poor...	Care in selection of soils has been found to be imperative and artificial drainage has frequently been found necessary.
Less than 1.2...	Bad....	Practically valueless for irrigation.

Hypothetical Combinations

The use of hypothetical combinations in the reporting of a mineral water is frequently of value, in that it gives a more rapid way of placing in simpler terms the principal materials present in the water. It should never be assumed from the hypothetical combinations that the materials so reported are present in the water in that particular form, but it is assumed by most, that the form in which such materials are reported will represent the condition in which those materials will combine when the water is subjected to increased pressure and increased temperature. In other words, the hypothetical combinations most generally in use represent the way materials will appear when combined, due to the law of mass action under steam-boiler conditions.

For such purpose the method which takes care of the insoluble materials or materials leaving the water first is the most common method in use. This method combines as follows: Where the sum of the sulphate and carbonate radicals exceeds that of lime and magnesia as bases, the magnesia is first calculated to carbonate, the remaining carbonate is combined with lime, the remaining lime

with sulphate and the remaining sulphate with sodium. This also takes care of the general condition where the carbonates alone are in excess of the combined carbonates of lime and magnesium, in which case the remaining carbonate naturally would be calculated to sodium and all the sulphate, as well as chloride, also, calculated to sodium. Where, however, the sum of the bases is greater than the sum of the carbonate and the sulphate radicals, two possible conditions or combinations exist. Where magnesium chloride is present in the water, the sum of the acids calculated to the soda radical should be greater than the total mineral residue. Partially decomposed magnesium chloride is indicated in this way, also the fact that magnesium chloride has a lower molecular weight than sodium chloride, which condition would be indicated in such a comparison. When this case exists, the sulphate is first calculated to calcium, the remaining calcium to carbonate, the remaining carbonate to magnesium, the remaining magnesium to chloride, the remaining chloride to sodium. Where the total mineral residue is greater than the sum of the acids and where nitrates are present, we then have nitrate of lime, which is assumed the commoner form than nitrate of magnesium, and the calculations are as follows: All the sulphate is calculated to lime, all the magnesium to carbonate, the remaining carbonate to lime, the remaining lime to nitrate, the remaining nitrate to sodium, and all the chlorides to sodium. In acid waters naturally the lime and magnesia, as well as the iron and aluminum, are calculated to the acid present in the greatest excess. These methods of calculation will give certain materials frequently found in scale formation and materials frequently supposed to cause certain characteristic troubles in either steam or domestic usage. It is possible in a purely qualitative way to judge or interpret the water on the basis of the lime and magnesium salts, for incrustation, and of the alkali salts for other troubles in boiler practice, also from the standpoint of irrigation, the various forms of the alkali salts as black and white alkali, without the necessity to use the formulas already considered.

Field Assay of Water

Mr. R. B. Dole has published in Water Supply Paper No. 151, of the U. S. Geological Survey, field methods for the assay of water in which tablets of known value are used for the determination of chlorides, carbonates, sulphates and iron. In this type of assay, a given amount of the water is taken and tablets are added to the water until certain definite reactions take place, when the number of tablets used is estimated and an approximate value obtained. The error in such work varies from 3 to 15 per cent, but the results of the test give valuable, if not accurate, information.

The author is indebted to Dr. F. E. Hale, Director of Laboratories Department of Water Supply, New York City, for a careful review of this chapter, and for valuable suggestions.

FIXED OILS, FATS AND WAXES

AUGUSTUS H. GILL[1]

It will be remembered that the *fixed oils* are those which leave a permanent stain on paper, whereas the essential or volatile oils evaporate. The fixed oils, if saponifiable, are glycerides of the higher fatty acids, oleic, $C_{17}H_{33}COOH$, stearic, $C_{17}H_{35}COOH$, palmitic, $C_{15}H_{31}COOH$; and if unsaponifiable, hydrocarbons, usually of the paraffin (C_nH_{2n+2}) and olefin (C_nH_{2n}) series. The *fats* differ from the oils in having a higher melting-point, caused by a larger percentage of stearic and palmitic acid. The *waxes* differ from the oils or fats in that the former are esters of monatomic alcohols. The oils are further divided according to their drying power on exposure to the air, into drying, semi-drying and non-drying oils.

The drying oils contain a large proportion of glycerides of the unsaturated acids, particularly linoleic and linolenic, whereas the semi-drying contain a smaller percentage, and the non-drying little or none of these esters.

Examination of an Unknown Oil

There being no specific tests for the various oils, as for their identification, the analyst should, in attacking an unknown oil, ascertain all possible facts about it, as the source, the use to which it is put, and the cost.

Certain physical properties too, may aid in the examination. The *color* is of little assistance, as oils may be colored by the use of oleates or butyrates of iron or copper. *Fluorescence* or "bloom" is valuable as indicating the presence of mineral oil; this can be shown by placing a few drops of the oil on a sheet of ebonite and observing the bluish color. The *odor* and *taste* are particularly valuable. Marine animal oils are detected, especially when warm, by their strong "fishy" odor, while neatsfoot, tallow, lard, rosin and linseed oils each have a well-marked and easily distinguishable smell. Whale oil is said to have a "nutty," and rape oil has a harsh, unpleasant "turnipy" taste. The *turbidity*, showing the presence of water, or of oils which imperfectly mix—as castor and mineral oils—and the *sediment*, either stearin or dirt, are also to be noted; these should be filtered out through paper before the oil is analyzed.

The **elaidin** test (page 582) may be applied next, to allow time for the cake to form; it will be followed by the **Maumené** test (page 582) both being done in duplicate. In making the elaidin test it is advisable to carry on an experiment under the same conditions with a known sample of lard oil. These two tests will show whether the sample under examination is a drying or non-drying oil and when the ingredients of the mixture are determined, the results of the Maumené test can be used for calculating their relative amounts. The **iodine** test can be employed to check this result.

[1] Professor of Technical Analysis at Massachusetts Institute of Technology, Cambridge, Mass.

The **saponification** test, unless mineral or rosin oil be suspected, need rarely be resorted to; the reason being that it would show practically nothing regarding the nature of the oil. Except in the case of castor (Sapn. No. 181), rape (174), sperm (135) and cocoanut (260), this characteristic is about 193.

Finally, where the importance of the case will warrant, the analyst is advised to prepare a mixture of oils using the proper proportions indicated by the various tests, and subject it to the more rapid tests as the specific gravity, viscosity, Maumené and iodine number. In making out the report of analysis it should be borne in mind that, excepting in the case of the special test, the results of *one* test cannot be relied upon to determine the nature of an oil, but the evidence of all the tests here given should be carefully compared and weighed before rendering a final verdict: in consideration of the fact of the wide variation of the characteristics of the oils, it is futile to report the quantities of oil found in a mixture more closely than 1%.

PETROLEUM PRODUCTS

(a) Burning Oils

The tests or determinations to be made are, in the order of their importance, flash, fire, specific gravity, distillation, sulphur, free acid, sulphuric acid, mineral salts and water. In some cases the color is determined.

Flash Test or Point. By flash point we understand the lowest temperature to which an oil must be heated, to give off vapors which when mixed with air produce an explosive mixture. The results of this test will vary according to the quantity of air over the surface of the oil, and whether this be moving or still; also according to the distance of the testing flame from the surface of the oil. Furthermore, the size of this testing flame, the length of its time of action, its form and dimensions, and lastly, the manner of heating the oil, will all influence the result.[1]

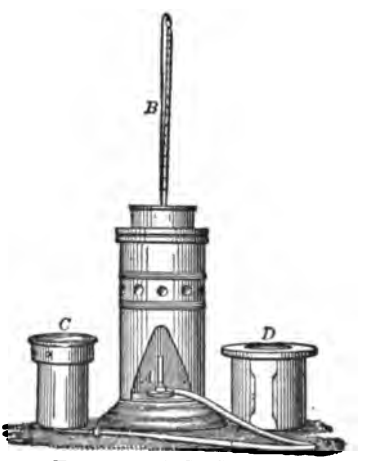

FIG. 86.—N. Y. Tester.

Any cause producing the rapid evolution of a large amount of petroleum vapor tends to lower the flash point. Barometric changes are, for practical work, negligible, each 5 mm. causing a variation of but 0.1° C.

Determination by the "New York State Board of Health Tester." The apparatus, Fig. 86, consists of a copper oil cup, *D*, holding about 10 oz., the quantity usually contained in lamps, heated in a water bath by a small Bunsen flame. The cup is provided with a glass cover, *C*, carrying a thermometer, *B*, and a hole for the insertion of the testing flame—a small gas flame one-quarter of an inch in length.

Manipulation. After describing the apparatus minutely, the regulations of

[1] Engler and Haase, Z. Anal. Chem., **20**, 3, 1881.

the New York State Board of Health say,[1] " (2) The test shall be applied according to the following directions:

" Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air-bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

" If an alcohol lamp be employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

" As a flash torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed linen twine. The flame in this case, however, should be small.

" When the temperature of the oil has reached 85° F. the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every two degrees' rise of the thermometer until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced if necessary and the testings continued for each two degrees.

" The appearance of a slight bluish flame which passes over the entire surface shows that the flashing-point has been reached.

" In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

" The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

For the determination with the open tester (Tagliabue's small) reference may be had to the author's " Short Handbook of Oil Analysis"; for the test with the closed tester, Abel's or Abel-Pensky, or Holde's "Examination of Hydrocarbon Oils " translated by Mueller.

Fire Test. The fire test of an oil is the lowest temperature at which it will give off vapors which when ignited will burn *continuously*. It is made by continuing to heat the oil (the cover being removed in the case of a closed tester without slipping out the thermometer) at the same rate after the flash test is made and noting the point as indicated above. The flame is extinguished by a piece of asbestos board and the heating discontinued. In the case of many illuminating oils this point is from 10° to 20° F. higher than the flash point.

In the case of " Mineral Sperm " (300° F. fire test oil) these tests should be made with the instrument for lubricating oils (page 576). The heating should be at the rate of 10° F. per minute, and the testing flame first applied at 230° F. and then every seven degrees until the flashing-point is reached.

The most satisfactory way of making these tests is to place the watch upon the desk and read the thermometer at the expiration of every minute, noting down each reading in the proper column in the laboratory note-book.

[1] Report of the New York State Board of Health, 1882, p. 495.

Specific Gravity: (*a*) ***By the Hydrometer.*** A hydrometer jar is four-fifths filled with the oil, a verified Baumé hydrometer introduced into it, and the depth read off to which the instrument sinks into the oil. This may be effected by placing a strip of white paper back of the jar and noting the point at which the lower meniscus of the oil touches the scale. The temperature of the oil is taken at the same time, and in case it be not 60° F. (15.5° C.), subtract 1° Baumé from the hydrometer reading, for every 10° F. it is higher than 60°, and add 1° Baumé for every 10° F. it is lower than 60° F. In practice this can be done by Tagliabue's "Manual for Inspectors of Coal Oil," which gives the readings at 60° F. for any gravity from 20° to 100° Baumé, between 20° and 109° F. The specific gravity may be found by the formula[1] $\frac{140}{130+B°}$, B° representing the reading Baumé at 15.5° C.

(*b*) ***By the Westphal Balance.*** This is a specially constructed instrument, Fig. 87, with a glass plummet carrying a thermometer counterbalanced by a weight. Upon immersing the plummet in a liquid the positions of the weights, which must be added to restore the equilibrium, represent the specific gravity directly. The largest weight represents the first decimal place, the next the second, and so on. The instrument is placed upon a level table, and by means of the leveling screw is brought into adjustment—i.e., so that the point upon the beam is exactly opposite the point upon the fixed part.

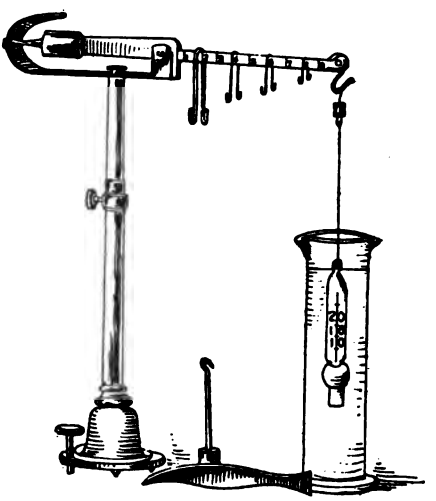

FIG. 87.—Wesphal Balance.

The plummet is now placed in the vial or balance jar containing the oil, cooled to 15.5° C., hung upon the balance, being careful completely to immerse it in the oil, weights added to restore the equilibrium, and the specific gravity read off as above described.

Care should be taken that the plummet does not touch the sides of the jar or vial. For solid fats and some oils the specific gravity is taken at 100° C., using a special plummet.

Distillation Test: Engler's Method. Engler uses a special boiling flask, 6.5 cm. in diameter, with neck 15 cm. long, and with the side tube about 9 cm. from the springing of the bulb; this is connected with a Liebig condenser and heated by a small lamp with a shield.

One hundred cubic centimeters of the oil are measured into the boiling flask and distilled at the rate of 2 to 2.5 cc. per minute, the distillate being caught in a 25-cc. burette or graduate. When the distillation is to be broken, the lamp should be taken away and the temperature allowed to sink 20° and again brought to the breaking or fractionating point, as long as any considerable quantity goes over. The distillation is first broken at 150° C., and then each 50° until 290°C.

[1] This formula applies to liquids lighter than water.

is reached; in this way a much better idea of the value of the oil is obtained than if the distillation were allowed to proceed continuously between these points. The lighter portions, for example, those between 150 and 200°, burn much better than those between 250 and 290°; the heavy portions of American petroleum burn much better than those of the Russian oils.

The averages from four samples of Caucasian and ten samples of American oils subjected to this test were as follows, in per cent by volume:[1]

	Below 150° C.	150–290°	Above 290° C.
Caucasian petroleum	8.0	86.6	5.4
American petroleum	16.9	57.1	26.0

Determination of Sulphur.[2] The deleterious effect of the oxides of sulphur upon hangings and bindings—as well as upon the human system—is well known, sulphuric acid being their ultimate product. The sulphur exists in combination, partly as compounds formed from the sulphuric acid used in refining and partly as alkyl sulphides. Its qualitative detection may be effected by heating the oil to its boiling-point with a bright piece of sodium or potassium. If sulphur compounds be present, a yellowish layer is formed upon the metal. After cooling add distilled water drop by drop until the metal is dissolved, and test for sulphides with sodium nitroprusside.

For the quantitative determination of sulphur 1 to 1½ grams of the oil are burned in a calorimetric bomb containing 10 cc. of water and oxygen under a pressure of 30 atmospheres. A lower pressure sometimes gives inaccurate results. If the sample contains more than 3% sulphur, the bomb is allowed to stand in its water bath for fifteen minutes after ignition of the charge. The bomb is allowed to cool fifteen minutes, opened, and its contents washed into a beaker. If the bomb has a lead washer, 5 cc. of a saturated solution of sodium carbonate is added, the contents are heated to the boiling-point, boiled for ten minutes and filtered. This is necessary to decompose any lead sulphate from the washer. The united washings are filtered and neutralized with HCl, using methyl orange as an indicator. The neutralized solution is poured into the tube of the Jackson turbidimeter,[3] diluted to near the 100-cc. mark, shaken, then acidified with 1 cc. of 1 : 1 hydrochloric acid, made up to the mark and mixed well by shaking. One of the barium chloride tablets is then dropped in[4] and the tube closed by a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity. When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; violent shaking should be avoided. The turbid liquid is transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a minute after each addi-

[1] Veith, "Das Erdoel," p. 244.

[2] Allen and Robertson, Technical Paper 26, Bureau of Mines; Chem. Abstracts, 6, 2997, 1912.

[3] Muer, J. Ind. and Eng. Chem., 3, 556, 1911.

[4] From the Frazer Tablet Co., Brooklyn, N. Y.; or 1 gram of barium chloride in dilute solution can be slowly added.

tion until the liquid in the tube is quiet, and continuing thus until the image of the flame just disappears. The depth of the liquid in centimeters is noted and the weight of sulphur found from the table on pages 676 and 677. The mixture is returned to the beaker, poured back and forth from beaker to tube two or three times and read again as before.

Or the barium sulphate can be determined in the usual way gravimetrically. In case a turbidity too low to be read with the apparatus be obtained, a larger quantity of oil must be used. Gasolines and light oils can be weighed out in a gelatin capsule.

The percentage of sulphur in a kerosene should not exceed 0.05; the Pennsylvania oils contain usually 0.02 to 0.03, the Lima 0.04 to 0.05.[1]

Detection of Acidity. Shake equal quantities of oil and warm water in a test-tube, pour off the oil, and test the water with litmus paper. If the water be strongly acid, the quantity may be determined as in "Free Acid," page 596.

The acid in this case is most probably sulphuric, coming from the refining process.

Sulphuric Acid Test. The object of this test is to judge of the degree of refinement of the oil, a perfectly refined oil giving little or no color when submitted to the process. One hundred grams of oil and 40 grams of sulphuric acid, 1.73 specific gravity, are shaken together for two minutes in a glass-stoppered bottle and the color of the acid noticed. For comparative work this color is matched by solutions of Bismarck brown.[2]

Mineral Salts. Salts of calcium or magnesium when dissolved in the oil diminish its illuminating power; their action is to form a crust on the wick and prevent access of air.

Redwood [3] states that 0.02 gram of either of these salts in 1000 grams of oil diminishes the illuminating power 30 to 40% in eight hours.

They are determined by distilling 100 to 200 cc. of the oil down to about 20 cc., evaporating and igniting this residue, and subsequently treating with hydrochloric acid. The calcium and magnesium are then determined in the usual way.

Determination of Water. By rubbing the oil together with a little eosin on a glass plate the oil will take on a pink color if water be present.

The evaporation method is approximate and applicable only to heavy oils and greases. Its accuracy even with heavy greases is questionable.

Dilute [4] the oil with an equal volume of benzol, whirl it vigorously in a centrifuge until the separated layer of water does not appear to increase in volume. However, as water is somewhat soluble in any diluent used and also in oils, a portion of the water content will fail to appear, consequently the method in which a diluent is used cannot be considered accurate. It is advisable first to agitate the diluent vigorously with water and then to separate with the centrifuge in order to saturate it with water before using.

Groschuff [5] states that 100 grams of benzene will dissolve 0.03 gram of water at 3° C. and 0.337 gram of water at 77° C., whereas petroleum products (density 0.792) will dissolve from 0.0012 gram at 2° C. to 0.097 gram at 94° C.

[1] Kissling, Ch., Rev. Fett und Harz. Ind., **14**, 157, 1906.
[2] J. Soc. Chem. Ind., **15**, 678, 1896.
[3] Dingler, Pol. J., **255**, 427, 1887.
[4] Reported by Allen and Jacobs. Bureau of Mines Technical Paper No. 25, 1912.
[5] Groschuff, E., "The Solubility of Water in Benzene, Petroleum and Paraffin in Oil," Chem. Abs., **5**, 2550, 1911.

While water to the extent even of 3 or 4% is apparently without influence on the viscosity, 1% extinguishes the flame when making the flash test.

Color. This test has lost its importance since oils are sometimes satisfactory despite their yellow color. The determination is usually made with the Stammer colorimeter in which the depth of the oil is changed in a cylinder until it matches the color of a standard plate of uranium glass. Standard white oil requires a depth of 50 mm. and water white from 300–320 mm. to match the color of the plate.

For a cut of the instrument and method of using, reference may be had to Holde's "Examination of Hydrocarbon Oils," translated by Mueller, page 52.

(b) Lubricating Oils

The tests to be made are, in the order of their importance, viscosity, specific gravity, evaporation, cold test, flash test, fire test, test for soap, carbon residue test, friction test. Saponification value, tarry matter insoluble in 88° naphtha, and added impurities are also determined.

The office of a lubricant is to prevent the attrition of axle and journal box by interposing itself between them in a thin layer, upon which the shaft revolves. The ideal lubricant is that which has the greatest adhesion to surfaces and the least cohesion among its own particles, or, as the practical man expresses it, the most fluid oil that will do the work and stay in place. The determination of its viscosity or "body" is then of the first importance.

Viscosity is the degree of fluidity of an oil or its internal friction. It is independent of the specific gravity of the oil, although this in the pipette instruments influences the time of efflux. Within certain limits it may be taken as a measure of the value of oil as a lubricant, by comparing the viscosity of the oil under examination with that of other oils which have been found to yield good results in practice.

The instruments employed for its determination may be divided into two classes—pipette viscosimeters, giving the time of efflux, as those of Engler, Saybolt, and others, and torsion viscosimeters, giving the retardation due to the oil, those of Macmichael and Doolittle.

In expressing viscosity, consequently, it is necessary to give the name of the instrument with which it is determined. It is sometimes expressed as specific viscosity, that is, the time of the oil divided by the time of water; this is only comparative when done with instruments of the same name, that is, specific viscosity Engler is not the same figure as specific viscosity Saybolt. Besides this manner of expressing viscosity, it is occasionally measured in absolute (C.G.S.) units or dynes. This is possible when the diameter of the orifice, its length, the quantity and specific gravity of the oil, its time of efflux and change of head are known. Where it is impracticable to determine all these data, by direct measurements, the readings of a viscosimeter may be changed into dynes by determining the viscosity in seconds of standard solutions of glycerine, the viscosity of these being determined in dynes from tables of physical constants. Or it may be done by use of the the tables on pages 575 and 608.

Engler Apparatus. *Description.* The apparatus (Fig. 88) consists of a flat, brass cylindrical vessel, *A*, 106 mm. in diameter and about 62 mm. deep, holding 240 cc., provided with a jet 2.9 mm. in diameter and 20 mm. long. This vessel is gilt inside and the jet, in the standard instruments, is of platinum—ordinarily it is made of brass; the vessel is surrounded with a bath, *B*, either of water or

oil, provided with a stirrer and heated by a ring burner. The jet is closed by the wooden valve, *F*, passing through the cover, and a thermometer, *c*, shows the temperature of the oil; three studs show the height to which *A* is filled and at the same time when it is level. The oil ordinarily is discharged into the 200-cc. flask, although in case the oil or time be limited, 100 or 50 cc. may be used and the time of efflux multiplied by a suitable factor. The instrument is standardized with water, 200 cc. of which at 20° C. should run out in from 50 to 52 seconds.

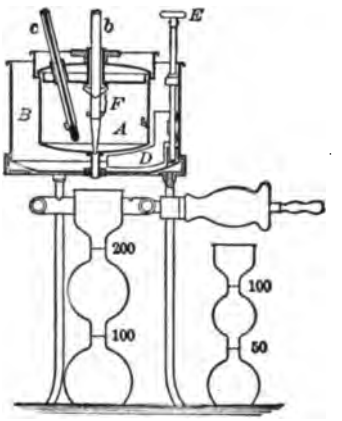

FIG. 88.—Engler Viscosimeter.

Manipulation. The instrument is thoroughly cleaned with alcohol and ether if necessary and dried; any suspended matter is removed from the oil, which is poured into it up to the level of the studs, stirred until 20° C. is reached and the bath adjusted to the same temperature. The flask is placed beneath the orifice, the plug raised and the time required for 200 cc. of oil to flow out is noted; this is divided by the water value of the instrument and gives then relative or specific viscosity. If only 50 cc. are allowed to run out the time must be multiplied by 5, and if 100 cc., by 2.35. If only 50 cc. were put in and 40 cc. allowed to run out, multiply this time by 3.62 to obtain the time for 200 cc.; if 66 cc. and 50 cc. run out, multiply by 2.79.[1] If it be desired to express the viscosity in absolute measure (C.G.S. units) it can be done by reference to the table on page 608. It should be noted that specific viscosity obtained with a different type of instrument, e.g., the Saybolt, is not the same as with the Engler.

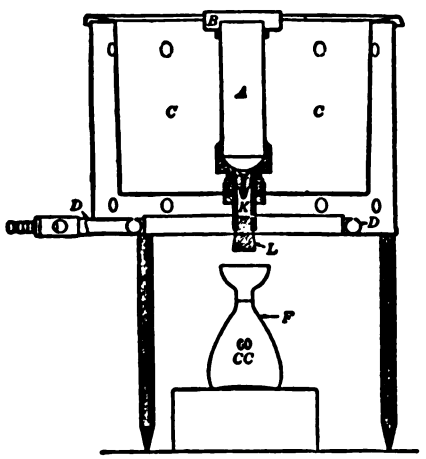

FIG. 89.—Saybolt Viscosimeter.

The Saybolt Viscosimeter.[2]— The Standard Universal Viscosimeter is the one now used for testing cylinder, valve, and similar oils at 210° F.; reduced black oils at 130° F.; spindle, paraffin, red, and other distilled oils at 100° F.

The Universal Viscosimeter. Description. This consists of a brass tube, *A*, forming the body of the pipette provided with a jet, *K*. The upper part of the pipette is surrounded with a gallery, *B*, which enables a workman to fill it to

[1] Gans, Chem. Revue der Fett und Harz. Ind., **6**, 221, 1899.

[2] Redwood, J. Soc. Chem. Ind., **5**, 124, 1886. This was formerly made in three forms, A, B, C. Apparatus "A" was the standard for testing at 70° F. Atlantic Red, Paraffin, and other distilled oils; "B" for testing at 70° F. Black Oils of 0°, 15°, 25°, and 30°, Cold Test, and other reduced oils up to, but not including, Summer Cold Test Oil. Apparatus "C" was used for testing at 212° F. Reduced, Summer, Cylinder, Filtered Cylinder, XXX Valve, 26.5° Bé., and other heavy oils.

the same point every time. The pipette is contained in a water bath, *C*, which can either be heated by steam or a ring burner, *D*; a tin cup with spout, a strainer, thermometer, pipette with rubber bulb, stop watch, and beaker for waste oil complete the outfit. It may be used for testing cylinder, valve, and similar oils with bath at 212° and oil at 210°; for testing reduced, black oils, bath and oil at 130°; for testing spindle, paraffin, red and other distilled oil bath and oil at 100°. When used for testing at 212° F., it may be used with either gas or steam alone or both in combination. If with both, the steam may be introduced slowly, more for its condensation to replace evaporation than for real heating purposes, depending upon the gas flame to reach the boiling-point, and keeping it there during the operation of test. The bath vessel should always be kept full during a test, whether at 212°, 130°, or 100°. When used at 130° or 100°, gas alone is used to bring the bath to the prescribed temperature, and turned off during the operation of test, the large size of the bath usually permitting making one test without reheating.

Its dimensions are as follows:[1]

Diameter of overflow cup	51.0 mm.
Depth of overflow cup	13.0 mm.
Diameter of pipette *A*	30.0 mm.
Depth from starting head to outlet jet	113.0 mm.
Length of outlet jet	13.0 mm.
Diameter of outlet jet	1.8 mm.
Capacity of pipette *A*	70 cc.

Manipulation. 1. Have the bath of water prepared at the prescribed temperature.

2. Have the oil strained into one of the tin cups, in which cup it may be heated up to about the standard temperature.

3. Clean out the tube with some of the oil to be tested by using the plunger sent with the instrument.

4. Place the cork (as little distance as possible) into the lower outlet coupling tube just enough to make air-tight, but not far enough to nearly touch the small outlet jet of the tube proper (one-eighth to one-quarter of an inch may be enough).

5. Pour the oil from the tin cup (again through the strainer) into the tube proper until it overflows into the overflow cup up to and above the upper edge of tube proper.

6. Now again see that the bath is at the prescribed temperature.

7. Use the thermometer sent with the instrument by stirring to bring the oil just to the standard temperature.

8. Remove the thermometer.

9. Draw from the overflow cup, with a pipette, all the surplus oil down to and below the upper edge of tube proper. This insures a positive starting head.

10. Place the 60-cc. flask under and directly in line with the outlet jet, and as close to the coupling tube as is practicable to permit of room for drawing the cork.

11. With the watch in left hand draw the cork with the right, and simultaneously start the watch.

12. The time required in the delivery of 60 cc. is the viscosity.

13. Clean out the tube proper before each test with some of the oil to be tested.

14. No drill or other instrument should ever be used in the small outlet jet of tube proper.

[1] Private communication.

The tube should be cleaned out before each test with some of the oil to be tested. Black oils or any oil containing sediment should be carefully strained before testing or "running," as it is technically termed. The instruments should be carefully guarded from dust when not in use.

The results obtained with this instrument are not the same in many cases as those furnished by the A, B, and C instruments, but they seem to have been adopted by the trade generally.

It is worth noting that 3 or 4% of water are apparently without influence on the viscosity.

Absolute Viscosity. This expresses viscosity in dynes, that is, the force necessary to produce the acceleration of 1 cc. per second on the mass of a gram. It is independent of the instrument used; Engler numbers can be converted to absolute viscosity by the following factors:

Engler No.	Absolute Viscosity Dynes per Sq.Cm.[1]
1	0.01006 × specific gravity
2	0.1146 × specific gravity
5	0.353 × specific gravity
10	0.726 × specific gravity
20	1.46 × specific gravity
30	2.19 × specific gravity
60	4.38 × specific gravity

The Engler numbers of 5 or over are quite nearly proportional to the absolute viscosities.

Specific Gravity. See under Burning Oils, page 569.

Evaporation Test.[2] The object of this test is to determine what percentage of an oil—more especially a spindle oil—is volatile when exposed to nearly the same conditions as it is on a bearing.

The oil is exposed upon annular disks of filter-paper 1⅝ in. outside diameter, with hole ⅝ in. in diameter, which have been standing in a sulphuric acid desiccator for several days, contained in a flat watch-glass.

Manipulation. The watch-glass and paper are weighed—to tenths of a milligram—and about 0.2 gram of oil brought upon it by dropping from a rod, and *accurately* weighed. The watch-glass is now placed in an air bath, the temperature of which remains nearly constant at 60° to 65° C. (140° to 150° F.), and heated for eight hours. It is then cooled and reweighed, the loss being figured in per cent. No oil should be passed which gives an evaporation of more than 4%.

The following table of results upon some spindle oils shows the relation of gravity, flash point, and evaporation:

Gravity.	Flash, °F.	Evaporation.	Gravity.	Flash, °F.	Evaporation.
.....	298	7.0%	.862	352	0.9%
.846	318	4.4%	.866	366	1.7%
.....	348	2.0%	.870	384	0.8%
.852	348	1.0%	.882	364	1.7%
.856	336	1.4%			

[1] Waidner, Proc. Am. Soc. Test. Mat., Pt. I, 293, 1915.
[2] Archbutt, J. Soc. Chem. Ind., 15, 326, 1896.

NOTES. The temperature employed, 65° C., is approximately that attained by a bearing (in a spinning frame) after running two hours, thus leaving the oil exposed to it for eight hours, assuming a ten-hour day.

The test is important to the insurance underwriter, because it measures the amount of inflammable material sent into the air, and hence the liability to cause or aid conflagrations; it is important to the mill-owner, as it indicates the quantity of oil left upon the bearing, hence serving its purpose.

The test is made upon other oils by heating them six hours in a shallow dish to 100°, 150°, 220, or 300°, sometimes in a draft of air.

Cold Test. This may be defined as the temperature at which the oil will just flow.

Manipulation. A 4-oz. vial is one-fourth filled with the oil to be examined, a short, rather heavy, thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, let it stand one hour; the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the bottle to the other. The reading of the thermometer is now taken by withdrawing it and wiping off the oil with waste to render the mercury visible.[1]

The chilling-point is the temperature at which flakes or scales begin to form in the liquid, and is determined similarly, by cooling the liquid 5° at a time.

Freezing Mixtures. For temperatures above 35° F. use cracked ice and water; between 35 and 0° F. use two parts of ice and one part of salt; and from 0 to −30° F. use three parts of crystallized calcium chloride and two parts of fine ice or snow. A still more convenient means is by the use of solid carbonic acid dissolved in ether, giving −50° F. readily.

The preceding method is open to quite an error from the personal equation of each observer. To obviate this Martens [2] proceeds as follows:

The oil is poured into a U-tube 1 cm. in diameter, 16 cm. high, with 3 cm. between the bends, to a depth of 3 cm.; it is then placed in a freezing mixture, cooled, and connected with a blast at a constant pressure of 3 cm. The temperature at which the oil begins to flow under these conditions is considered as the cold test.

Flash Point. Several forms of apparatus for testing the flash point of lubricating oils have been devised: Pensky-Martens's closed tester employing a stirrer is used in Germany. Martens states in a later article that stirring is unnecessary. In this country an open cast-iron or spun brass cup—the Cleveland open cup—$1\frac{3}{8}$ in. high by $2\frac{1}{2}$ in. in diameter, heated by a Tirrill burner in an air bath is quite extensively used. Dudley and Pease use an open porcelain dish heated with a Bunsen burner.

The cup, Fig. 90, is filled with oil to about $\frac{1}{4}$ in. from the top and the thermometer is suspended so that the bulb is just immersed in the oil. The oil is heated at the rate of 10° F. a minute by a Bunsen burner with a protecting chimney; as the flash point is approached, a test is made for every rise of 3° by slowly passing the small bead-like test flame across the cup near the thermometer. The oil should flash near the thermometer when the proper point is reached. The fire test is, as a rule, 50° to 80° F. higher than the flash point. As the open-cup tests are easily affected by drafts, they are subject to errors of 5° F. The thermometers used should be compared with a standard

[1] Dudley and Pease, An. Eng. and R. R. J., **69**, 332, 1895.

[2] Mitt. kgl. tech. Versuchstation; abstr. J. Soc. Chem. Ind., **9**, 772, 1890.

ıd corrected for stem exposure. When this is done it is suggested that " corr. " ɜ added to the reading: thus, " flash 379° F. corr."

Fire Test. The cover is supported above the cup, and the heating and ɔplication of the testing flame continued as in making the flash test.

The method of recording is the same as in the case of the illuminating oils, ıe column for times and another for temperatures. Holde [1] finds that with oils

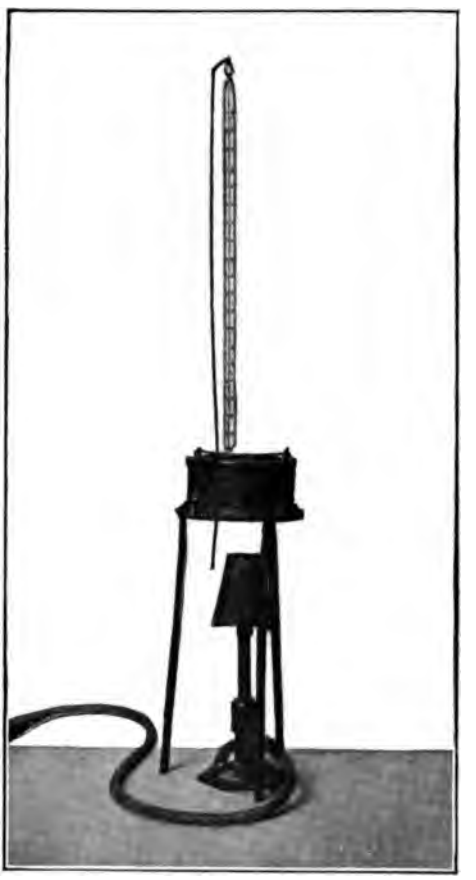

FIG. 90.—Cleveland Cup.

shing between 172° C. and 241° C. the exact quantity of oil used is of little portance. In these particular cases a difference of filling of 13 cc. altered the sh point only 1–1.5° C. For the effect of water see page 572.

It is worthy of notice that the free fatty (oleic) acid contained in an oil lowers flash point apparently in proportion to the quantity present.

[1] J. Soc. Chem. Ind., **16**, 322, 1897.

Detection of Soap. To increase the viscosity of an oil,[1] resort is had to the use of "oil pulp," "oil-thickener," or "white gelatin," usually an oleate of aluminum, though other bases may be present. Its disadvantages are that it causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminum are insoluble in absolute alcohol.[2]

The test is applied as follows: five to 10 cc. of the oil to be tested are dissolved in about 5 cc. of 86° gasoline or ether, and about 15 drops of the phosphoric acid solution (Appendix, Reagents) added, shaken and allowed to stand; the formation of a flocculent precipitate indicates the presence of soap. An idea of the kind of soap can be often gained by adding an alcoholic solution of $PtCl_4$. If the precipitate becomes crystalline it is a potash soap; if it dissolves, soda, lime, or magnesia; if unchanged, alumina or iron.

For the accurate determination of these compounds a known weight of the oil must be ignited, the residue determined and quantitatively examined.

Caoutchouc. Holde [3] states that 1 to 2% of unvulcanized caoutchouc is sometimes added to oils to increase their viscosity. This may be detected by adding three parts of alcohol to four parts of the ethereal solution, whereby the rubber material is precipitated and may be dried and weighed.

Test for Fatty Oils. To detect small quantities of fatty oil (½ to 2%) Lux[4] recommends heating a few cubic centimeters of the oil for fifteen minutes with some bits of sodium in a test-tube in an oil bath; a similar test is made with sodium hydrate. The temperature employed should be for light oils about 230°, for dark oils 250°.[5] In case fatty oil be present, the contents of one or both of the tubes solidify to a jelly of greater or less consistence according to the amount of fatty oil present.

The quantitative determination of these oils, as for example in cylinder oils, is effected after the manner of determining the saponification value (page 587) or the detection of unsaponifiable oils in fatty oils (page 588).

Schreiber [6] adopts a method similar to Sweetham and Henriques, in that he dissolves 5 grams of the oil in 25 cc. of benzole, adds 25–50 cc. N/2 alcoholic potash, and boils for half an hour on the water bath, using a 3-ft. glass tube as a condenser.

Gumming Test.[7] This is designed to give an idea of the amount of a change that may be expected in a mineral oil when in use. These resinified products increase the friction of the revolving or rubbing surfaces.[8] It is also a measure of the amount that an oil will "carbonize" in a gas or gasoline engine cylinder. It is applied after the manner of the elaidin test, by thoroughly mixing together 5 grams of the oil in a cordial glass with 11 grams of nitrosul-

[1] In a case which came to the writer's notice the oil would not flow out of the Saybolt "A" apparatus at 70°, at 85° required 1167", and at 110°, 181."
[2] Schweitzer and Lungwitz, J. Soc. Chem. Ind., **13**, 1178, 1894.
[3] "Examination of Hydrocarbon Oils," p. 166.
[4] Z. anal. Chem., **24**, 357, 1885.
[5] Holde, Untersuchung d. Schmieröle u. Fette, p. 175.
[6] J. Am. Chem. Soc., **29**, 74, 1907.
[7] Gill, J. Am. Chem. Soc., **24**, 467, 1902.
[8] Aisinman, J. Soc. Chem. Ind., **14**, 282, 1895.

phuric acid and cooling by immersion in a pan of water at 10–15°. Brownish spots or, in case of a bad oil, masses, form around the edges and become red in the course of two hours. The cordial glass is filled successively three times with 70–86° naphtha and the oil dissolved off the surface of the acid, the gasoline solution being sucked off into a bottle with an air pump. Care is taken not to suck off any of the tarry matter formed. The acid can be neutralized with ammonia and the tar can be collected on a tared filter, washed with gasoline that leaves no residue on evaporation, dried at a low temperature, and weighed as gummy matter. As shown by long practical experience, the oil showing the least tar or gum is the best oil; it also absorbs the least oxygen.

Carbon Residue Test. ***Gray's Method.*** To a tared 1-oz. quartz flask of the dimensions shown in Fig. 91, add 25 cc. of the oil to be tested and weigh. Wrap the neck of the flask with asbestos paper as far down as the side arm. Stopper tightly with a good cork. Connect to a small aerial condenser by plugging the space with asbestos or glass wool. Provide a shield which will protect the flame and the flask up to the side tube. Using the flame of a good Bunsen or Tirrell burner, heat the flask so that the first drop of distillate will come over in approximately five minutes. Continue the distillation at such a rate that 1 drop per second will fall from the end of the condenser. As the end of the distillation approaches, increase the heat just enough so that no heavy vapors are allowed to condense and drop back into the flask; continue increasing the heat until the flask is enveloped in the flame, and hold the temperature five minutes. Allow the flask to cool, remove the asbestos covering and cork, and burn out completely the carbon and oil in the neck as far down as the side tube, and in the side tube. Heat the bottom of the flask until no more vapors are given off. Cool and weigh.

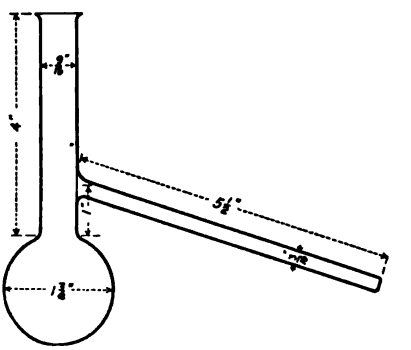

FIG. 91.—Gray's Distillation Flask.

Motor oils, of light and medium grade, range in coke-like residue from 0.06 to 0.5%, the percentage offixed carbon being roughly proportional to the viscosity of the oil. That is, the higher the viscosity, the higher will be the percentage of fixed carbon, provided the oils have been manufactured from the same grade of crude petroleum by the same general methods. The heavy and extra heavy motor oils range from 0.5 to 1.25%. As the percentage of fixed carbon varies with the viscosities of the oils, the viscosity should be taken into consideration. For illustration, it would not be fair to compare a motor oil having a viscosity of 200 at 100° F., Saybolt, with a motor oil having a viscosity of 400 at the same temperature. The carbon residue in the 200 viscosity oil would be in the neighborhood of 0.2%, where as the fixed carbon of the higher viscosity oil would be in the neighborhood of 0.75%.

Gasoline Test. This shows the presence of tar (still bottoms) or asphaltic matters.

Mix 10 cc. of the oil with 90 cc. 86°–88° gasoline (from Pennsylvania crude) B.pt. 30°–50° C., allow to stand one hour at 70° to 80° F.; not more than 10% of flocculent or tarry matter should have settled out. This settling can be

facilitated by whirling in a centrifuge in a graduated tube in which the volume of the precipitate can be read off. If the test be applied to the oil before making the flash test and then again after this test it shows the extent to which the oil is changed upon heating. Other things being equal the oil which is changed the least is the best oil.[1]

Microscopical Test. Put a few drops of the well-mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffin which disappear on warming, or foreign matter. A good oil should be practically free from all these bodies.

Friction Tests. The writer is inclined to doubt if friction tests are worth the outlay for a machine and the time expended in their execution. Without question they do determine the relative efficiency as regards lubricating power of different oils, but the conditions under which the test is made seldom occur in practice; the bearings upon which the oil is tested are as nearly perfect as can be made, and the feed and load are as regular as is possible; in other words, the conditions are ideal.

The lubricating power of an oil is so closely related to its viscosity[2] that the author believes that results of more practical value can be obtained by the determination of the viscosity of the oils, and subsequent observation of their behavior in actual use than by the longer and more troublesome friction test. Recent experiments,[3] however, have shown that of two oils of the same viscosity and other constants the coefficient of friction of one was 14% less than the other.

In case, however, it be desired to make the friction test, the following machines, it is believed, will be found to be most satisfactory for the purpose:

For spindle oils and light lubricating oils, the machine[4] of the Thurston type which can be run at the highest speed and lowest pressure.

For heavy oils and railroad work, the large machine of the Thurston[5] type, described in his "Friction and Lost Work in Machinery and Millwork," page 254; also in Brannt, page 486; also in Archbutt and Deeley.[6]

For machines using a flooded bearing the Beauchamp-Tower machine, described in the "Proceedings of the Institution of Mechanical Engineers of Great Britain," 1883, 632; 1884, 29; 1885, 58; 1888, 173; 1891, 131; also in Archbutt and Deeley.[7]

ANIMAL AND VEGETABLE OILS

The tests most commonly employed for the identification of these oils are as follows: specific gravity, refractive index, Valenta test, elaidin test, Maumené test, iodine number, and saponification value.

In addition, certain special and commercial tests are applied, as Bechi test, Baudouin test, free acid, spontaneous combustion, and drying test.

Specific Gravity. This is usually determined either by the Westphal balance (page 569) or by the *picnometer*.

[1] Conradson, J. Ind. and Eng. Ch., **2**, 171, 1910.
[2] Brannt, "Petroleum and its Products," p. 510; Woodbury, *vide infra*.
[3] Trans. Am. Soc. Mech. Eng., **32**, 834, 1910.
[4] Made by Olsen or Riehlé Bros., Philadelphia, Pa.
[5] "Lubrication and Lubricants," 1907, pp. 332–348.
[6] Ibid., p. 359.
[7] Ibid., p. 355.

A two-necked flask of 50 cc. capacity, having a thermometer carefully ground into one neck, the second one being a narrow tube bearing the mark, is most suitable. This is filled with the oil to be examined, cooled to 15.5° C.,[1] the excess of oil removed and weighed. If the weighings be made to 0.5 milligram and a correction applied for the expansion of the glass by the difference in temperature = 15.5 − 4 = 11.5° = −0.025% of the value obtained, the determination is accurate to 0.00002.[2]

For the determination of the specific gravity of small quantities of oil, satisfactory results can be obtained by weighing 1 or 5 cc. of the oil carefully measured from an accurately calibrated pipette. Or a mixture of alcohol and water can be made until a drop of oil will stay in any position in it, and its specific gravity determined.

Refractive Index. This is of the same value as the determination of specific gravity: it has, however, the advantage that it is more rapid and uses only one or two drops of the oil.

The apparatus preferably employed is the Abbé refractometer, Fig. 92, the prisms of which are kept at constant temperature, usually 25° C., by circulating water.

The illuminating mirror should light the cross hairs and the telescope should be sharply focused on them.

The double prism is opened by means of the screw heads, and after carefully cleansing the prisms with cotton and ether, a drop or two of the oil placed on the horizontal surface of the fixed prism. The prisms are then tightly closed. The telescope is brought into the position shown and the sector is firmly held and the alidade (the moving part) moved forward until the field of vision shows the boundary between light and shade just intersecting the cross hairs.

By means of the screw on the right of the instrument this boundary line should be made as sharp as possible. The index of refraction is read off directly from the sector, using a lens if necessary; the reading is accurate to .0002.

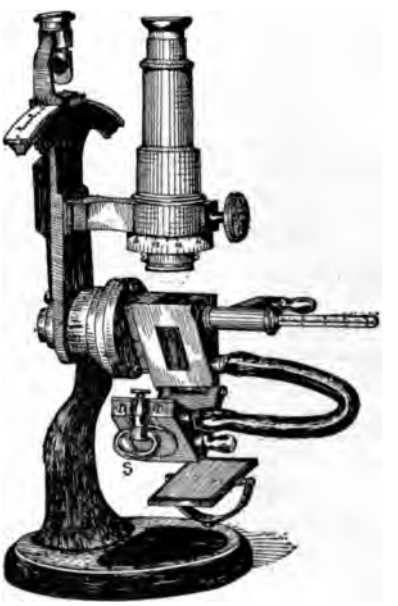

FIG. 92.—Refractometer.

After using, the prisms are again carefully cleansed and a piece of filter paper placed between them to prevent them from being scratched. The instrument is in correct adjustment when water at 18° gives a mean reading of 1.333. The temperature correction for oils and fats is 0.0004 for every degree rise.

Valenta Test.[3] Although considered by some to be unreliable, yet as the

[1] Allen (Organic Analysis, 33) states that a correction of 0.00064 can be made for each variation of 1° C.

[2] Wright, J. Soc. Chem. Ind., **11**, 300, 1892.

[3] Valenta, Dingler polyt. J., **253**, 418; also J. Soc. Chem., Ind., **3**, 643, 1884.

indication given by this test may be of value, it is barely worth the trouble of execution. It depends upon the solubility of the oil in glacial acetic acid.

Enough oil is poured into a test-tube to fill it to the depth of about 1 in., the exact height being marked by the thumb; an equal quantity of glacial acetic acid is poured in, that is, until the acid reaches the point indicated by the thumb. A light thermometer is placed in the tube, and it is heated until the oil dissolves —shown by the liquid becoming homogeneous. The tube is now allowed to cool, and the point noted at which it begins to become thoroughly turbid.

Castor oil is soluble at ordinary temperatures, while rape-seed and other cruciferous oils are usually insoluble even at the boiling-point of the acid. The temperatures at which other oils become turbid are given on pages 604 and 605.

Elaidin Test. Although this is not a quantitative test, yet its ease of application and the conclusions which may be drawn from it render it valuable. It depends upon the change of the liquid olein into its solid isomer elaidin, and is especially applicable to olive and lard oils.

Manipulation. Five grams of the oil are weighed [1]—within 2 drops—into a cordial glass, 7 grams of nitric acid, specific gravity 1.34, are then weighed into it,[1] and two pieces of copper wire (0.6 to 1.0 gram) added. Place the glass in a pan of cold water at about 12° C., and stir with a short glass rod about 20 to 30 turns, not only with a rotary movement, but also with an up-and-down motion, so as to mix the oil and the evolved gas thoroughly. When the wire has dissolved, add a second piece and stir as before. This second addition should furnish gas enough if the liquid has been kept cool and the stirring has been thorough.

At the end of the first hour, pure lard oil will usually show flakes of a wax-like appearance, and upon standing without disturbance and at the same temperature for another hour, the oil will have changed to a solid white cake hard enough to bear several ounces' weight, or admit of lifting the glass and contents by the glass rod.

Most of the fish and seed oils yield a pasty or buttery mass separating from a fluid portion, whereas olive, almond, peanut, lard, sperm and sometimes neat's-foot oil, yield a solid cake.

Instead of using nitric acid and copper, sulphuric acid of 46° Baumé, containing a little nitric acid and saturated at 0° C. with nitric oxide, may be employed.

A test should always be made at the same time with an oil of undoubted purity.

NOTES. If the oil be stirred too much or too frequently, or is too warm, it has no opportunity to form a hard cake.

Hübl states that all attempts to make the test a quantitative one have resulted in failure.

Mercury can be used instead of copper.

Cailletet's method,[2] in which a smaller quantity of oil is used, and sulphuric and nitric acids allowed to act upon it in a boiling water bath, cannot, in the experience of the writer, be depended upon to give reliable results.

Maumené Test.[3] While this, like the preceding, is not a quantitative test, yet the indications afforded by it are of more value in many cases than those obtained by quantitative methods, as, for example, the saponification value. It depends upon the heat developed by the mixing of the oil with strong sul-

[1] Not on the analytical balance.

[2] Milliau, J. Am. Chem. Soc., **15**, 156, 1893.

[3] SO_2Cl gives similar results.

phuric acid. This takes place in a small beaker 7½ to 9 cm. deep and of 150 cc. capacity, packed in an agate-ware cup with dry felt or cotton waste packing.

Manipulation. Fifty grams of the oil are weighed [1] into the beaker to within 2 drops, and its temperature noted by a thermometer. Ten cc. of sulphuric acid are now run gradually into the oil—allowing the graduate to drain five seconds—the mixture being stirred at the same time, and the stirring continued until no further increase in temperature is noted. The highest point at which the thermometer remains constant for any appreciable time is observed, and the difference between this and the initial temperature is the "rise of temperature." This varies with the strength of the acid employed, and to secure uniformity [2] the results should be expressed by dividing the rise of temperature with the oil by the rise of temperature with water, and multiplying by one hundred. This is called the "specific temperature reaction." The rise of temperature with water is determined in the same manner as with oil, using the same vessel.

NOTES. In performing this test it is important that the oil and acid be of the same temperature, attained by keeping them beside each other.

The strength of acid should be as far as possible the same; it should be determined not by specific gravity, but by titration, as 100% and 94.3% acid have the same specific gravity.

For concordant results the conditions should be the same, and the same apparatus should be used. In case the test is to be applied to a drying oil, it should be diluted one-half with a mineral oil, 25° paraffin, for example, thoroughly mixing them. The "rise of temperature" is then, the rise of temperature of mixture minus half the rise of temperature of 50 grams of mineral oil, multiplied by 2.

It is advisable to make a test at the same time with an oil of known purity. Results should agree within 2%. By the use of the Hübl formula, page 586, substituting thermal values, results comparable with those obtained with the iodine value can be obtained.

Sherman, Danziger, and Kohnstamm [3] have studied this method with the idea of eliminating the errors. Rather than dilute the oil with a mineral oil they dilute the acid, using one of 89%. The results obtained are a little lower for vegetable oils and a little higher for animal oils than those usually found with the strong acid as employed by Thomson and Ballantyne. Mitchell [4] uses an inert diluent—carbon tetrachloride—in a vacuum-jacketed tube and one-fifth the quantities; all oils are diluted. He finds that the results obtained are in close agreement with the bromine thermal values; further, that the test may be of use in determining the degree of oxidation of fats and oils, the figures becoming greater with the age of the oil.

Data upon various oils will be found on pages 603–605.

References.

Maumené, Compt.-Rend., **35**, 572, 1852.
Ellis, J. Soc. Chem. Ind., **5**, 361, 1886.
Thomson and Ballantyne, J. Soc. Chem. Ind., **10**, 234, 1891.
Richmond, Analyst, **20**, 58, 1895.
Munroe, Am. Pub. Health Ass'n, **10**, 236, 1884.

Iodine Number or Value. This is the percentage of iodine absorbed by an oil; the method depends upon the fact that different oils absorb different amounts of the halogens; the process is mainly one of addition, although small quantities

[1] Not on the analytical balance.
[2] Tortelli, J. Soc. Chem. Ind., **23**, 668, 1904, is unable to secure uniformity in this way.
[3] J. Am. Chem. Soc., **24**, 266, 1902.
[4] Analyst, **26**, 169, 1901.

of substitution products are formed. For example, the unsaturated body olein, $(C_{17}H_{33}COO)_3C_3H_5$, when brought in contact with iodine takes up 6 atoms and forms the ***addition product,*** di-iodo stearin, $(C_{17}H_{33}I_2COO)_3C_3H_5$. Palmitin, $(C_{15}H_{31}COO)_3C_3H_5$, when similarly treated, forms no addition product, but a small quantity of the ***substitution product,*** iodo-palmitin, $(C_{15}H_{30}ICOO)_3C_3H_5$, and the hydrogen displaced unites with the iodine to form hydriodic acid. The quantity of hydriodic acid thus formed is a measure of the amount of substitution.[1]

1. ***Hanus's Method.*** *Manipulation.* From 0.12 to 0.15 gram of a drying oil, 0.2 to 0.3 gram of a non-drying oil, or 0.6 to 0.7 gram of a solid fat, is accurately weighed into a ***dry*** 200-cc. bottle. This should be of colorless glass and be provided with a well-ground stopper. This is best effected by pouring out about 5 grams of the oil into a No. 1 beaker containing a short stirring rod, and setting it into a watch-glass upon the pan of the analytical balance. The whole system is weighed, the beaker removed, and several drops of oil transferred to the bottle by dropping down the rod, being careful that no oil touches the neck. Eight drops are approximately 0.2 gram. The beaker is replaced in the watch-glass and the system again weighed, the difference in weight being the amount of oil in the bottle.

The oil is dissolved in 10 cc. of chloroform, 30 cc. of the iodine solution (Reagents) added—best from a burette—and allowed to stand with occasional shaking for exactly fifteen minutes; with oils of an iodine number of less than 100, ten minutes suffices; 15 cc. of potassium iodide solution [2] are added and the solution titrated, with or without the addition of starch, with sodium thiosulphate until the halogen disappears.

At the same time at which the oil is prepared, two "blanks" should be prepared similarly in every way to the actual tests, except in the addition of the oil, and treated in every respect like them; the strength of the thiosulphate solution should also be determined the same day on which this test is carried out.

Standardization of the Thiosulphate Solution. Ten cc. of potassium iodide and 100 cc. of water are poured into the Erlenmeyer flask; 20 cc. of the bichromate solution, equivalent to 0.2 gram of iodine, are now measured in with a pipette, and to this 5 cc. of strong hydrochloric acid added and the mixture shaken for three minutes. It is now titrated with the thiosulphate solution until the yellow color of the iodine has almost disappeared; starch paste is now added, and the titration continued until the deep-blue color of the solution changes to a sea-green due to $CrCl_3$,— which is usually brought about by the addition of a single drop.

The reactions involved are:

$$K_2Cr_2O_7+14HCl=2CrCl_3+2KCl+7H_2O+3Cl_2;$$

$$3Cl_2+6KI=6KCl+3I_2;$$

$$6Na_2S_2O_3+3I_2=3N_2S_4O_6+6NaI.$$

NOTES. Wijs [3] uses iodine chloride instead of bromide; it is more troublesome to prepare and gives results about 1.2 points higher.[4] Either of these methods has the advantage over Hübl's -first, that the solutions keep better, remaining practically

[1] McIlhiney, J. Am. Chem. Soc., **16**, 275, 1894.

[2] This is the original method. Tolman adds here 100 cc. water as in the Hübl method.

[3] Berichte, **31**, 752, 1898.

[4] Tolman and Munson, J. Am. Chem. Soc., **25**, 244, **1903.**

unchanged for several months; secondly, that the action is about sixteen times as rapid, it being completed in fifteen minutes; thirdly, that the solutions are cheaper.

Acetic acid cannot be displaced by carbon tetrachloride as a solvent, as the last traces of iodine are difficult to remove from it. The acetic acid used should be at least 99.5% and show no reduction with potassium bichromate and sulphuric acid.

2. ***Hübl's Method.*** *Manipulation.* The oil is weighed out as in 1, into 300-cc. bottles, except that about 25% more may be used.

The oil is now dissolved in 10 cc. of chloroform, 30 cc. of iodine and mercuric chloride solution added, the bottle placed in a dark closet, and allowed to stand, with occasional gentle shaking, for four hours. If the solution becomes nearly decolorized after two hours, an additional quantity should be added. One hundred cc. of distilled water and 20 cc. of potassium iodide are added to the contents, and the excess of iodine titrated with sodium thiosulphate. If at this point a red precipitate (HgI_2) is formed, more potassium iodide should be added. As the chloroform dissolves some of the iodine, the titration can proceed until the chloroform layer is nearly colorless, then the starch solution is added, and the operation continued to the disappearance of the blue color.

" Blanks " should be titrated as with the foregoing process, page 584.

NOTES. The method was proposed by Cailletet in 1857, made use of by Mills and Snodgrass [1] in 1883, using, however, bromine and carbon bisulphide, and described in almost its present form by Hübl.[2] The chief factors in its execution are (1) strength of the iodine solution; (2) the quantity used; and (3) the length of its time of action.

1. *The Strength of Iodine Solution.* According to Hübl's original memoir, the solutions can be kept indefinitely when mixed.

Fahrion [3] states that the solution deteriorated as much as from 17 to 23% in eight days. Ballantyne [4] confirms the deterioration, but finds it much less, 5 to 8% in thirty-eight days. This weakening of the solution is probably due to the hydriodic acid formed by the action of the iodine upon the alcohol.[5]

The mercuric chloride acts apparently as a carrier of iodine, as the reaction takes place very slowly without it. (Gantter.) [6] Waller [7] finds that the addition of 50 cc. HCl, specific gravity, 1.19, to the mixed iodine solution preserves it for months. Of the other metallic chlorides, $CoCl_2$ gives the highest true iodine value, $MnCl_2$, $MnBr_2$ and $NiCl_2$ cause practically no addition. (Schweitzer and Lungwitz.) [8]

2. *The Quantity of Iodine Solution Used.* The mixed iodine solution as made up should require about 53 cc. of the thiosulphate. Before using, a rough titration should be made, and if it be much weaker than this, a proportionately larger amount added. The action of a large excess of iodine is to increase the substitution rather than addition; increase in temperature or in time produces the same effect.[9]

The excess of iodine recommended is from 150 to 250%; some observers recommend from 400 [10] to 600%.[11]

3. *Length of Time.* Two hours is sufficient for olive oil, tallow, and lard, while for linseed oil, balsams, and resins twenty-four hours should be allowed.[12]

[1] J. Soc. Chem. Ind., **2**, 435, 1883.
[2] Dingler polyt. J., **253**, 281; also J. Soc. Chem. Ind., **3**, 641, 1884.
[3] J. Chem. Ind., **11**, 183, abstr., 1892.
[4] Ibid., **13**, 1100, abstr., 1894.
[5] J. Soc. Chem. Ind., **14**, 130, 1895.
[6] Ibid., **12**, 717, abstr., 1893.
[7] Chem. Ztg., **19**, 1786, 1831, 1895.
[8] J. Soc. Chem. Ind., **14**, 1031, 1895.
[9] J. Soc. Chem. Ind., **12**, 717, abstr., 1893.
[10] Ibid., **14**, 1031, 1895.
[11] Holde, Mitt. kgl. Techn. Versuchs., **9**, 81, 1891.
[12] Dieterich, J. Soc. Chem. Ind., **12**, 381, 1893.

Ingle[1] has shown that the free acid formed during the process is due to the action of water upon the iodochlorides. Some of these are reduced by potassium iodide with liberation of iodine and consequent reduction in the iodine absorption. Iodine chloride is the active agent, and not hypoiodous acid.

For the calculation of the percentage of adulteration of one oil by another, Hübl gives the following formula:[2]

"Let x = percentage of one oil and y = percentage of the other oil, further, m = iodine value of pure oil x, n of pure oil y, and I of the sample under examination, then

$$x = \frac{100(I-n)}{m-n}."$$

He further states that the age of the oil, provided it be not rancid or thickened, is without influence on the iodine value. Ballantyne[3] finds that light and air diminish the iodine number.

As might be expected, the iodine value is inversely proportional to the cold test.

The method, as will be seen, is a conventional one, and the best results will be obtained by using measured quantities of reagents and carrying through the process in the same manner every time.[4]

The calculation is perhaps most easily made as follows: Subtract the number of cc. of thiosulphate used for the titration of the oil, from that obtained by titrating the blank—this gives the thiosulphate equivalent to the iodine absorbed by the oil. Multiply this number (of cc.) by the value of the thiosulphate in terms of iodine, and the result is the number of grams of iodine absorbed by the oil; this divided by the weight of oil used and multiplied by 100 gives the iodine number.

In case it be desired to recover the iodine used, reference may be had to an article by Dieterich, abstracted in the Jour. Soc. Chem. Ind., **15**, 680, 1896.

Oxidized Oils. Iodine Number of. To find the original iodine number of a semi-drying or non-drying oil which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity $\left(\text{taken at } \frac{15.5°\text{ C.}}{15.5°\text{ C.}}\right)$.[5]

Bromine Number or Value. The iodine method just described has, among others, the disadvantage that it fails to distinguish between addition and substitution; this is sometimes of importance, and to accomplish it McIlhiney[6] makes use of the bromine absorption.

Manipulation. From 0.2 to 0.3 gram of a drying oil, 0.4 to 0.5 of a non-drying oil, or 1.0 to 1.2 grams of a solid fat, are accurately weighed into the 300 cc. bottle, as in the iodine number (page 584).

The oil is dissolved in 10 cc. of carbon tetrachloride, and 20 cc. of bromine solution (Reagents) added, best from a burette. After allowing it to stand two minutes by the watch, 20 or 30 cc. of potassium iodide are added, in the manner

[1] J. Soc. Chem. Ind., **21**, 587, 1902.
[2] Dingler polyt. J., **253**, 281, 1884.
[3] J. Soc. Chem. Ind., **10**, 31, 1891.
[4] If, for example, the water be added before the iodide solution, the iodine number is changed by 0.3 per cent.
[5] Sherman and Falk., J. Am. Chem. Soc., **27**, 608, 1895.
[6] J. Am. Chem. Soc., **21**, 1084, 1899.

described below, the amount depending upon the excess of bromine. To prevent loss of bromine and hydrobromic acid, a short piece of thin and wide rubber tubing—" bill tie tubing "—is slipped over the lip of the bottle, thus forming a well around the stopper; some of the iodide solution is poured into this and the bottle cooled in cracked ice. Upon removing the stopper the solution is sucked into the bottle, it is shaken to insure the solution of the vapors, and the remainder of the reagent added. The iodine liberated is titrated by sodium thiosulphate in the usual way.

When this titration is finished, 5 cc. of the potassium iodate solution are added and the titration repeated. The iodine liberated in this reaction is equivalent to the hydrobromic acid present. Blank determinations should be made with the reagents used, as with the iodine number.

NOTES. Oftentimes, particularly with resins, emulsification of the solution takes place, masking the end-point. This can be prevented by the addition of 50 or 100 cc. of a 10% solution of salt.

In case ice be not at hand, the vapors will probably be completely absorbed by passing through the iodine solution in the rubber well.

The reactions involved, in addition to those on page 584 are:

$$\overset{\text{Palmitin}}{(C_{15}H_{31}COO)_3C_3H_5} + 3Br_2 = (C_{15}H_{30}BrCOO)_3C_3H_5 + 3HBr.$$

$$3HBr + 3KI = 3KBr + 3HI.$$

$$6HI + KIO_3 = 3I_2 + 3H_2O + KI.$$

The calculation is similar to that followed in the iodine number (page 584).

The percentage of bromine found as hydrobromic acid is called the bromine substitution figure, and the total percentage absorbed, less twice the bromine substitution figure, gives the bromine addition figure.

The method has the further advantages that it is rapid, the bromine solution is permanent and inexpensive. For data upon various oils, see table on page 604.

Saponification Value. This is expressed by the number of milligrams of potassium hydrate necessary to saponify one gram of the oil. It is called from the originator " Koettstorfer [1] number or value," also " Saponification number," and must not be confounded with " Saponification equivalent " as proposed by Allen,[2] which is the number of grams of oil saponified by 56.1 grams of potassium hydrate.

Manipulation. One to 2 grams of the oil are weighed out into a 200-cc. Erlenmeyer flask (as in the iodine value, *q. v.*, page 584) and saponified by 25 cc. N/2 alcoholic potash accurately measured from a burette, by heating upon a water bath, a 1-in. funnel being inserted in the flask.

When the saponification is complete, shown by the homogeneity of the solution, a few drops of phenolphthalein are added and the excess of alkali titrated with N/2 hydrochloric acid. Two blank determinations of the strength of the N/2 potassium hydrate must be made simultaneously, by heating 25 cc. under the same conditions as when mixed with the oil and for the same length of time.

NOTES. Many prefer to cork the flasks tightly and tie down the stoppers, thus saponifying under pressure; others make use of a return flow condenser, oftentimes merely a long glass tube.

Smetham [3] adds 20 cc. of ether and finds that it aids saponification. Henriques [4]

[1] Z. anal. Chem., 18, 199, 1879.
[2] Commercial Organic Analysis, 2, 40.
[3] Analyst, 18, 193, 1893.
[4] Z. angew. Chemie, 721, 1895.

uses 3 to 4 grams of oil, 25 cc. of petroleum ether, and 25 cc. of *normal* alcoholic potash, saponifying in the cold by allowing to stand overnight; the advantage consists in preventing the change in the solution by boiling.

McIlhiney [1] has applied the process to dark-colored substances by making use of the principle that when ammonium chloride is added to a neutral soap solution, and the mixture distilled, the amount of ammonia freed is equivalent to the quantity of alkali combined with the fatty acids. As a description of the process is beyond the scope of the present volume, reference must be had to the original article.

As ordinarily prepared, the alcoholic potash solution turns rapidly reddish-brown, so that it is very difficult to note the end-point. This trouble can be partially avoided by adding a drop or two of the solution to the diluted indicator contained upon a tile after the manner of the titration of iron by bichromate. As the color is probably due to the polymerization of the aldehyde formed by the oxidation of the alcohol, it is more satisfactory to use for the preparation of the potash solution an alcohol which is practically aldehyde free. This is best made, according to Dunlap,[2] as follows: 1½ grams of silver nitrate are dissolved in 3 cc. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 cc. of warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled. Alcoholic potash made up from this, using the so-called "potash by alcohol," will give a solution which will remain water-white for weeks.

The writer has found, if the stock solution be kept under an atmosphere of hydrogen, that the coloration by standing is almost entirely prevented.

Detection of Unsaponifiable Oils. The qualitative detection takes place by observing the behavior of the solution obtained by boiling the oil with alcoholic potash when diluted with warm water. Any unsaponifiable material will manifest itself as oily drops in the clear alcoholic solution, or as a whitish cloud on the addition of water.

The quantitative determination may take place in two ways: 1. From the saponification number. 2. By gravimetric methods.

1. ***From the Saponification Number.*** On pages 604 and 605 it will be noticed that, except for castor, rape, and sperm oils, the saponification number averages 193. If the number found be divided by this figure, the percentage of saponifiable matter will be obtained; this subtracted from 100 will give the unsaponifiable matter. This method gives no idea of the kind of saponifiable matter.

2. ***By Gravimetric Methods.*** The procedure is essentially that of Spitz and Hönig:[3] 10 grams of the oil are boiled fifteen minutes under a return-flow condenser with 50 cc. of 5% alcoholic potash;[4] 40 cc. of water are added and the boiling repeated. The liquid is allowed to cool, washed into a separatory funnel with 50% alcohol and 50 cc. of 86° gasoline, thoroughly shaken and allowed to stand. The gasoline layer should separate clearly and quickly from the soap solution and the latter is drawn off; the gasoline is washed 2 or 3 times with 50% alcohol to extract any soap, and these washings added to the soap solution. This latter is extracted, until upon evaporation the gasoline leaves no stain upon paper, care being taken to wash the gasoline extracts each time with 50% alcohol; three extractions with gasoline are usually sufficient.

The gasoline is distilled from these extracts, the residue heated until the gas-

[1] J. Am. Chem. Soc., 16, 409, 1894. For a discussion of the theory of the process, see Lewkowitsch, J. Soc. Chem. Ind., 17, 1107, 1898.

[2] J. Am. Chem. Soc., 28, 397, 1906.

[3] Z. ang. Chem., 19, 565, 1891.

[4] The potash is made by dissolving purified potash in the smallest possible quantity of water and adding absolute alcohol.

oline odor disappears, and weighed. From the appearance of the residue some idea of the kind of unsaponifiable matter can be obtained. This in the case of sperm oil will be mainly solid alcohols, probably of the ethylene series.

According to Schicht and Halpern [1] this method is open to the following errors: incomplete saponification, incomplete extraction, solubility of soaps in the solvent, and the solubility of the unsaponifiable matter in the washing solution. Their improved method is as follows: 5 grams of fat [2] with 3 of grams solid caustic potash dissolved in a little water and 25 cc. of absolute alcohol are boiled half an hour under a reflux condenser. After cooling 25 cc. of 10% KCl are added and the solution is then shaken four times with 200 cc. of petroleum ether distilling under 60°. The petroleum ether is evaporated and, without washing, the residue is dissolved in 25 cc. absolute alcohol and the solution made slightly alkaline with normal alkali; 25 cc. of 10% KCl are added and the shaking with petroleum ether repeated. The petroleum ether solution is shaken with 100 cc. of 50% alcohol and the wash solution with 100 cc. petroleum of ether, which is afterwards washed with 100 cc. of 50% alcohol. After combining the extracts the petroleum ether is driven off and the residue dried and weighed.

NOTE. Care should be taken to use gasoline which leaves no residue on evaporation at 100° C.

Identification of the Unsaponifiable Matter. The unsaponifiable matter is either liquid or solid; in case it is liquid, it may be (1) *hydrocarbon oils*, either mineral, or formed by the distillation of waste fats, as wool grease, or (2) *tar oils*, "dead oils," etc., obtained by the distillation of coal tar; or (3) *rosin oils*.

If it be a question of one of these three, the specific gravity will usually decide it; that of the hydrocarbon oils is 0.855 to 0.930, of the rosin oils 0.96 to 0.99, while the tar oils are heavier than water. Rosin oils would be shown by the Liebermann-Storch test, page 595; a mixture of mineral and tar oils would be identified by treatment with an equal quantity of nitric acid, sp.gr. 1.45, both previously cooled to 15° C., and noting the rise of temperature. Mineral oils give a very slight rise, being paraffins, while the tar oils belong to the benzole series and are more easily nitrated. Hydrocarbon oils from distilled grease oleins can be identified by their refractive index and rotatory power.[3]

Solid unsaponifiable matters may be:

(4) *Paraffin.*

(5) *Ceresene*—refined ozokerite.

(6) *Higher alcohols* of the paraffin series, as cetyl, $C_{16}H_{33}OH$, coming from the saponification of sperm oil and other waxes.

(7) *Cholesterol*, $C_{25}H_{43}OH$, and its isomers, phytosterol, sitosterol, isocholesterol, etc.

(8) *Lactones*, internal anhydrides of oxy acids as stearlactone,

$$C_{14}H_{29}CHOHCH_2CH_2COOH = C_{14}H_{29}\underbrace{CHCH_2CH_2COO}+H_2O.$$

These may be separated by boiling for two hours with an equal quantity of acetic

[1] Chem. Ztg., 31, 279, 1907.

[2] For linseed and other oils, ten or twenty times this weight should be used, the alkali being correspondingly increased.

[3] Gill and Forrest, J. Am. Chem. Soc, 32, 1071; Gill and Mason, J. Am. Chem. Soc., 26, 665.

anhydride; if the substance dissolves and does not precipitate on cooling, higher alcohols are indicated; if a mass of crystals separates out on cooling, cholesterol and its isomers, or a mixture of these with the higher alcohols is indicated; if an oily layer remains on top, it is an indication of the presence of paraffin or ceresene. For the complete separation and identification of these reference must be had to Lewkowitsch, " Analysis of Fats, Oils, and Waxes," as it is beyond the limits of this chapter.

Test for Animal or Vegetable Oils. Animal oils contain cholesterol, $C_{26}H_{43}OH$, while vegetable oils contain the isomeric body phytosterol; hence the isolation and identification of these compounds enables one to say with certainty as to the presence of one class of oil or the other—for example as to the presence of fish oil in linseed. The quantity of these bodies varies from 0.2 to 1%. The method is essentially that of Bömer.[1] Fifty grams of the oil are boiled in a flask with a return cooler with 75 cc. of 95% alcohol for five minutes and the alcoholic solution separated; this is repeated with another portion of alcohol. The alcoholic solutions are mixed with 15 cc. of 30% sodium hydroxide and evaporated on a water bath nearly to dryness in a porcelain dish and the residue shaken out with ether. The ether is evaporated, the residue taken up with a little ether, filtered, again evaporated, dissolved in 95% alcohol (by volume), and allowed to crystallize slowly. Bömer states that the form of the crystals is more to be relied upon than a determination of their melting-point. Cholesterol crystallizes from alcohol or ether in leaflets or rhomboid tables containing one molecule of water of crystallization. Phytosterol crystallizes also from alcohol with one molecule of water in needles forming stars or bundles. As a further means of identification, some of the esters should be made and their melting-points determined.

To this end the crystals above obtained are heated over a low flame in a small porcelain dish covered with a watch-glass, with 2 or 3 cc. of acetic or other acid anhydride until it boils: the watch-glass is removed and the excess of anhydride evaporated on the water bath. The contents of the dish are treated with a small quantity of absolute alcohol to prevent crystallization, more alcohol added and the solution allowed to crystallize. The crystals are filtered off through a very small filter, washed with a small quantity of 95% alcohol, dissolved in absolute alcohol, and recrystallized until a constant melting-point is obtained.

The following table shows the corrected melting-points of these alcohols and their esters:

	Cholesterol.	Phytosterol.
Alcohol	148–150.8°	136–143.8°
Acetate	113–114°	120–137°
Benzoate	135–151°	142–148°
Propionate	97–98°	104–105°

NOTES. Some directions state, in isolating the cholesterol or phytosterol, to boil with the 30% sodium hydroxide until one-fourth of the alcohol is evaporated. As a result of repeated experiments this has been found to cut down the yield so much that on a large scale practically none of these bodies, particularly phytosterol, was obtained. This agrees with the observation of Lewkowitsch that by heating cholesterol with normal alcoholic potash, cholesterin hydrate is obtained.

The following test will serve to differentiate between cholesterol and phytosterol.[2] A very small quantity of cholesterol is warmed with 1.5 cc. absolute alcohol and a

[1] J. Soc. Chem. Ind., 17, 954, 1898; Tolman, J. Am. Chem. Soc., 27, 590, 1905; nan, Bull. 107, U. S. Dept. Agriculture, 1907.

Neuberg and Rauchwerger, abstr. J. Soc. Chem. Ind., 23, 1163, 1904.

trace of isodulcit or rhamnose (δ-dimethylfurfural) added. After cooling, an equal volume of concentrated sulphuric acid is added, so as to form a layer below the solution, whereupon a raspberry-colored ring is produced at the zone of contact of the two liquids. On mixing the layers while the tube is cooled in a current of cold water the mixture becomes intensely colored. With phytosterol the reaction fails or at most a pink color. Similar reactions are given by abietic acid.

As little as 1% of cotton-seed has been found in lard, and 4% in any oil have been detected by this test.

For the means of distinguishing between drying and marine animal oils, see Halphen, J. Pharm. Chim., 14, 391 (1901), abstracted J. Soc. Chem. Ind., 21, 74, or Chem. Centralb., 72, ii, 1097 and 1323.

Tests for Antifluorescents.[1] It is often desired to remove the fluorescence or " bloom " from petroleum oils. This may be effected by refining with chromic acid, or more easily by the addition of a small quantity of nitro-naphthalene or nitro-benzene. The latter may often be detected by the odor.

The test is made by boiling about 1 cc. of the oil with 3 cc. of 10% alcoholic potash for one to two minutes. If either of the nitro compounds be present, a blood- or violet-red coloration is produced; a pure mineral oil is changed only to yellow or brownish-yellow by this treatment. In case the characteristic color does not appear the following test may be applied.[2] It depends upon the reduction of the nitro bodies to their amines.

A few cc. of the oil are heated with feathered tin and hydrochloric acid in an Erlenmeyer flask for ten minutes: this can be aided by the introduction of a piece of platinum wire. The oil is separated by a separatory funnel and filtration through a wet filter, the filtrate treated in another separatory with sodium hydrate until the tin hydrate redissolves and shaken out with 10–20 cc. of ether. The amines go into solution in the ether, giving to it a violet color and fluorescence in the case of α-naphthylamine. These can be recognized by their odor, that of naphthylamine being very characteristic. The latter may be recognized by dissolving in hydrochloric acid, evaporating the latter, and upon treatment with ferric chloride obtaining an azure-blue precipitate. This changes when filtered off to purple-red and the filtrate to violet.

Aniline can be recognized by solution in concentrated sulphuric acid and the red and then blue color which appears on the addition of a small crystal of potassium bichromate. Free aniline is also temporarily colored violet by a solution of bleaching powder.

Acetyl Value. The estimation of the acetyl value is seldom required in oil analysis, it being characteristic only when triglycerides are present. For a description of the method and its applications, reference must be had to the larger works, as Lewkowitsch or Allen.

Special Tests for Certain Oils

Lewkowitsch says[3] " It should be distinctly understood that color reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test. The ease with which this test can be carried out, and its apparent reliability, have led to an over-estimation of this very useful and important reaction; so much

[1] Holde, J. Soc. Chem. Ind., 13, 906, 1893.
[2] Holde, " Examination of Hydrocarbon Oils," p. 168.
[3] " Chemical Technology and Analysis of Fats, Oils and Waxes," 2, 203.

so, that grave errors may be committed by those who assign to this test an exclusive or even a paramount importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation."

Bechi's Test for Cotton-seed Oil. This depends upon the supposition that a substance of an aldehydic nature which reduces silver nitrate is contained in the oil. The method is essentially that of Milliau.[1]

Fifteen grams of oil are weighed into a No. 6 porcelain dish, using the coarse scales, and heated for about ten minutes upon the water bath; a mixture of 10 cc. of 30% caustic soda and 10 cc. of the alcohol is slowly poured upon the oil. The whole is occasionally stirred until the mass becomes clear and homogeneous, and 150 cc. of hot distilled water slowly added so as not to decompose the soap, and the boiling continued until the alcohol is expelled. Dilute sulphuric acid (1:10) is added to acid reaction, and the separated fatty acids washed three times by decantation with cold water. A portion of these is brought into a large test-tube, 15 cc. of alcohol and 2 cc. of 3% silver nitrate solution are added, the tube is wrapped with brown paper, held in place by an elastic band, and heated, with constant stirring, in the water bath until one-third of the alcohol is expelled, which is replaced by 10 cc. of water. This heating is continued for a few minutes longer and the coloration of the insoluble fatty acids observed. The presence of cotton-seed oil in any appreciable proportion causes a mirrorlike precipitate of metallic silver, which blackens the fatty acids of the mixture.

NOTES. The alcohol should be proved free from aldehyde by a blank test. Unless the mixture in the test-tube be thoroughly stirred while heating, it will "bump" and eject the contents. Other methods of procedure consist in applying the test to the oil itself, often after treatment with dilute caustic soda and nitric acid. (Wesson.[2]) The writer had a case in which the *oil* gave the test while the *fatty acids* gave no blackening, showing there was something in the oil itself other than cotton-seed oil which reduced the silver nitrate. Students have no difficulty in detecting a 5% adulteration with cotton-seed oil.

Dupont [3] thinks that the reduction of silver nitrate is due rather to sulphur compounds contained in the oil; by passing steam over the oil he obtained a product containing sulphur and the oil still gave the Bechi test. This work has been repeated and confirmed by the author.[4] It is to be noted that while the fatty acids blacken silver nitrate they do not color cadmium, lead, or copper salts, but reduce mercury compounds. No indication of an aldehyde was noted by the fuchsine or ammonia tests. The supposition that the reducing substance is aldehydic in its nature finds support in the fact that if the oil be heated to 240° [5] or be kept for some time [6] it loses this peculiar property.

By purifying the acids by the lead salts Tortelli and Ruggeri [7] are able to detect as little as 10% of heated cotton-seed oil.

It is to be noted that pure lard, tung and olive oil are not infrequently met with which give the test, consequently its indications cannot be considered as conclusive.

Halphen's Test for Cotton-seed Oil.[8] This depends upon the observation

[1] J. Am. Chem. Soc., **15**, 164, 1893.
[2] J. Am. Chem. Soc., **17**, 723, 1895.
[3] Bull. Soc. Chem. (3), **13**, 696; J. Soc. Chem. Ind., **14**, 811, 1895; also Charabot and March, Bull. Soc. Chim., **21**, 252, 1899.
[4] Gill and Dennison, J. Am. Chem. Soc., **24**, 397, 1902.
[5] Holde, J. Soc. Chem. Ind., **11**, 637, 1892.
[6] Wilson, Chem. News, **59**, 99, 1889.
[7] J. Soc. Chem. Ind., **20**, 753, 1901.
[8] Halphen, J. Pharm. Chim., 390, 1897.

that this oil contains an unsaturated fatty acid which combines with sulphur, giving a colored compound.[1]

Procedure. Ten cc. of the oil or melted fat are heated, in a large test-tube with a long glass condenser tube attached, with an equal volume of amyl alcohol and of carbon bisulphide solution of sulphur (Reagents), at first with frequent agitation, in a steam bath, and then, after the violent boiling has ceased, in a brine bath (105–110°) for forty-five minutes to three hours, according to the quantity of adulterant present, the tube being occasionally removed and shaken. As little as 1% will give a crimson wine coloration in twenty minutes.[2]

NOTES. If the mixture be heated for too long a time a misleading brownish-red color due to burning is produced. The reaction seems to be peculiar to this oil; it is more sensitive with fresh than old fats, and while, by comparison with a blank, $\frac{1}{10}$ of 1% is noticeable, $\frac{1}{4}$ of 1% is easily detected. Cotton-seed oil which has been heated to 250° does not give the test; the oil is then not available as food. Heating to 200° does not interfere with the test.[3]

The test is not given by an oil which has been oxidized with sulphuric acid and potassium permanganate, although such an oil gives the Bechi test.[4] This shows that the two tests are not produced by the same substance. Nor is this test or that of Bechi given by an oil which has been treated with chlorine or sulphurous acid.[5] If treated with the former it is no longer edible; an oil treated with sulphurous acid and washed with alcohol cannot be distinguished from ordinary cotton-seed oil and does not, as already stated, respond to either the Halphen or Bechi test. In this case the test for phytosterol is the only means of determining if it has been added to an animal oil. The test is also given by kapok oil, which is used as an edible oil in China, the East and West Indies, and in Africa; baobab oil also gives it.

Lard from hogs fed on cotton-seed meal shows this reaction strongly, as if it were 25% oil.[6] The butter from cows similarly fed also yields the reaction.[7]

The test may be applied to the soaps or fatty acids, provided they are not too deeply colored.

The amyl alcohol cannot be omitted nor substituted by ethyl alcohol without impairing the delicacy of the test.[8] The compound in the oil cannot be removed by treating with animal charcoal.[9]

Hexabromide Test for Linseed Oil. The object of the test is to determine the amount of insoluble bromides of the fatty acids contained in the oil.

Fifteen grams of the oil are saponified by boiling with 15 cc. of potassium hydroxide solution, sp.gr., 1.35, and 15 cc. of alcohol in a flask under a reflux condenser; 300 cc. of warm water are added and the solution distilled with steam until the alcohol is removed. Dilute sulphuric acid is added to excess, the solution heated until the fatty acids are obtained as a clear oily upper layer; this is washed several times with hot distilled water until free from sulphuric acid, using methyl orange as an indicator. This does not react with fatty acids of low molecular weight which being soluble in water may redden litmus. This washing is effected in an atmosphere of inert gas, carbonic acid or hydrogen by stopping the flask with a three-holed stopper, carrying a siphon, an entrance and an exit tube for the gas.

[1] Raikow, Chem. Ztg., **24**, 562, 583, 1900.
[2] Oilar, Am. Chem. J., **24**, 355; abstr Anal., **26**, 22, 1901.
[3] Fischer and Peyan, Analyst, **30**, 131, 1905; Soltsien, Z. öffentl. Chem., **5**, 135. 1899; J. Soc. Chem. Ind., **18**, 865.
[4] Raikow, loc. cit.
[5] Petkow, Analyst, **32**, 123, 1907.
[6] Soltsien, Z. öffentl. Chem., **7**, 140, 1901.
[7] Wauters, J. Soc. Chem. Ind., **19**, 172, 1900.
[8] Soltsien, loc. cit., **25**, Oilar, loc. cit.
[9] Utz, Rev. Fett u. Harz. Ind., **9**, 125, 1902.

The acids are siphoned into a small Erlenmeyer flask and in case a few drops of water come over—an equal quantity of alcohol added and dried upon the water bath in a stream of dry inert gas.

In order to test for the presence of unsaponified fat, 3 cc. are dissolved in 15 cc. of 95% (by volume) alcohol, and 15 cc. of aqueous ammonia are added. If an appreciable amount of fat has escaped saponification, the mixture will become turbid (Geitel).

Two grams of mixed fatty acids [1] are dissolved in a flask in 27 cc. of dry ether, cooled down to 10° C., and 0.25 cc. of bromine allowed to run into the solution from a very finely-drawn-out pipette, the time allowed for this being about twenty minutes. The remaining 0.25 cc. of bromine is added somewhat more rapidly, within about ten minutes, the bromination thus occupying about thirty minutes. The authors attach great value to the exact observance of the time. The temperature should never be allowed to rise during bromination above 5°. The flask is corked and allowed to stand for two hours at 0°. The ethereal solution is next decanted through a weighed asbestos or paper filter (Lewkowitsch) and the precipitate is washed with five lots of 5 cc. each of dried and cooled ether. After complete draining, the precipitate is dried for two hours at 80° to 85°, and allowed to cool in a desiccator. The temperature is designedly kept below 100°, as the authors found that the color of the hexabromide becomes somewhat gray if the drying takes place at 100°. The melting-point of the hexabromides was 177°, whereas the melting-point of pure hexabromide has been found to be higher. No doubt the low melting-point is due to the drying having been carried out below 100°.

Nevertheless small traces of retained moisture cannot account for the much larger yield of hexabromide which the authors obtained.

The yields of hexabromide obtained by these authors are as follows:

Fatty Acids	Per cent.	Fatty Acids	Per cent.
Perilla oil	64.12	Tung oil	nil
Linseed oil, Baltic	57.96	Soya bean oil	up to 7.78
Linseed oil, Dutch	51.73	Poppy seed oil	nil
Linseed oil, La Plata	51.66	Rape oil	6.34
Linseed oil. Indian	50.50		

Renard's Test for Peanut Oil.[2] Tolman [3] has modified this as follows:

Weigh 20 grams of oil into an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash into a 500-cc. flask containing a boiling mixture of 100 cc. of water and 120 cc. of a 20% lead acetate solution. Boil for a minute and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, the water and excess of lead can be poured off and the soap washed with cold water and with 99% (by volume) alcohol. Add 200 cc. of ether, cork, and allow to stand for some time until the soap is disintegrated, heat on the water

[1] Eibner and Muggenthaler, Farben Ztg., 1912.
[2] Renard, Compt. rend., **73**, 1330, 1871; also Archbutt, J. Soc. Chem. Ind., **17**, 1124.
[3] Bull. 107, U. S. Dept. Agriculture, 1907, p. 145.

ath, using a reflux condenser, and boil for about five minutes. In the oils most f the soap will be dissolved, while in lards, which contain much stearin, part ill be left undissolved. Cool the ether solution of soap to 15° or 17° C. and et it stand until all the insoluble soaps have crystallized out (about twelve ours).

Filter and thoroughly wash the precipitate with ether. Wash the soaps on he filter back into the flask by means of a stream of hot water acidified with ydrochloric acid. Add an excess of dilute hydrochloric acid, partially fill the ask with hot water, and heat until the fatty acids form a clear oily layer. Fill the ask with hot water, allow the fatty acids to harden and separate from the precipitated lead chloride, wash, drain, repeat washing with hot water, and dissolve he fatty acids in 100 cc. of boiling 90 per cent (by volume) alcohol. Cool to 5° C., shaking thoroughly to aid crystallization.

From 5 to 10 per cent of peanut oil can be detected by this method, as it ffects a complete separation of the soluble acids from the insoluble, which interere with the crystallization of the arachidic acid. Filter, wash the precipitate wice with 10 cc. of 90% (by volume) alcohol, and then with alcohol 70% (by volme). Dissolve off the filter with boiling absolute alcohol, evaporate to dryness n a weighed dish, dry and weigh. Add to this weight 0.0025 gram for each 10 cc. f 90% alcohol used in the crystallization and washing if done at 15° C.; if done t 20° add 0.0045 gram for each 10 cc. The melting-point of arachidic acid thus btained is between 71° and 72° C. Twenty times the weight of arachidic acid ill give the approximate amount of peanut oil present. No examination for dulterants in olive oil is complete without making the test for peanut oil. Arahidic acid has a characteristic structure and can be detected by the microscope.

Bach's Test for Rapeseed Oil. According to O. Bach,[1] the acids obtained from ape-seed oil are completely insoluble in David's alcoholic acetic acid, in the roportion of 1 to 15, by volume; those from cottonseed, peanut, sesame, and unflower oil dissolve on heating. Those from the last oil separate as a granular recipitate at 15°, while from the other three they gelatinize. The acids from live oil are completely soluble at the ordinary temperature. David's acid is ade by mixing 22 cc. of 50% acetic acid (by volume) with 30 cc. of alcohol, sp.gr. .817, 92.07% (by weight.)

NOTE. The author has found that Bach's observation cannot be implicitly elied upon, as some rape-seed oils yield acids which are soluble in David's mixture.

Liebermann-Storch Test for Rosin Oil. One or 2 cc. of the oil are shaken ith an equal quantity of acetic anhydride and gently warmed. When cool he acetic anhydride is pipetted off and tested by the addition of 1 drop of conentrated sulphuric acid. A fine violet color is produced in the presence of rosin il. Tung oil and also cholesterol, which is contained in the animal fats, produce similar coloration; the latter can be removed by saponifying the oil as completely s possible and shaking out the somewhat dilute soap solution with ether or etroleum ether. The soap solution is then acidified, setting free the fatty cids, and these treated with acetic anhydride as if they were the oil.

Baudouin's, or Camoin's test for Sesamé Oil. Villavecchia and Fabris[2] pply the test as follows: 0.1 gram sugar is dissolved in 10 cc. of hydrochloric acid

[1] Allen, " Commercial Organic Analysis," 2, pt. 1, 128, 1899.
[2] Z. angew. Chem., 509, 1892; abstr. J. Soc. Chem. Ind., 12, 67; also Kerp, Analyst, 4, 246, 1899.

of specific gravity 1.18 in a test-tube, and 20 grams of the oil to be tested added, the whole thoroughly shaken and allowed to stand. In the presence of 1% of sesamé oil the aqueous liquid will be colored red,[1] due to the action of the furfurol formed upon the oil. They state that as olive oils of undoubted purity have shown the reaction in the aqueous layer and not in the oily stratum, the color should be looked for in the latter.

The sugar may be replaced by 0.1 cc. of a 2% solution of furfurol and half the quantity of oil used.

Milliau[2] saponifies as in the Bechi test and dries the acids at 105°. Lewkowitsch[3] states that this is a needless complication. Da Silva[4] states that this test has given colors with certain Portuguese olive oils; also those of Bari Brindisi and Lecce. Kreis[5] states that the active or color-giving constituent is probably phenolic in its nature. The reaction is given by other substances,[6] as vanillin, oil of cloves, and cinnamon; this should be borne in mind in testing oils which have been extracted from confectionery. Rancid fats prevent the coloration; it can, however, be brought about even in rancid fats by the addition of an equal quantity of cotton-seed oil.[7]

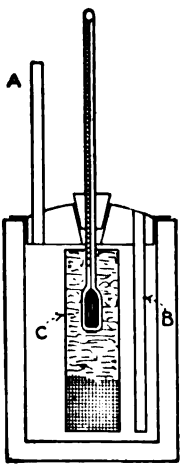

FIG. 92a.

Mackey's Apparatus.

Free Acid Test. About 10 grams of oil are weighed (to centigrams) into a 250-cc. Erlenmeyer flask, 60 cc. of neutral alcohol (Reagents) added, the mixture warmed to about 60° C., and titrated with N/6 potassium hydrate, using phenolphthalein, the flask being frequently and thoroughly shaken. The result is conventionally reported in per cent of oleic acid: 1.0 cc. N/6 KOH is equivalent to 0.047 gram oleic acid. Or it can be reported like the saponification number, in milligrams of KOH per gram of oil.

Spontaneous Combustion Test. Mackey's Apparatus. The apparatus,[8] Fig. 92*a*, consists of a cylindrical copper water bath 7 in. high and 4 in. in diameter (inside measurements), surrounded with a ½-in. water-jacket. The cover is packed with asbestos and carries the draft tubes *A* and *B*, ½ in. in diameter and 6 in. long, which cause a current of air to be sucked down *B* and up *A*, thus ensuring a circulation of air in the apparatus: *C* is a cylinder made of 24-mesh wire gauze 6 in. high and 1½ in. in diameter and supported upon a projection from the bottom of the bath. A thermometer projects down into the center of the cylinder; if a metal condenser be connected to the water bath it can be used indefinitely without refilling and without danger of burning out.

Seven grams of ordinary bleached cotton wadding or "absorbent cotton" are weighed out in a porcelain dish or on a watch-glass, and 14 grams of the oil to be tested poured upon the cotton and thoroughly worked into it, care being

[1] Ibid., 1893, 505; abstr. Analyst, **19**, 47.
[2] J. Am. Chem. Soc., **15**, 162, 1893.
[3] "Oils, Fats and Waxes."
[4] J. Soc. Chem. Ind., **17**, 275, 1898.
[5] Chem. Ztg., **27**, 316, 1903.
[6] Gerber, Analyst, **32**, 90, 1907.
[7] Lauff and Hinsmann, Chem. Ztg., **31**, 1023, 1908.
[8] Mackey, J. Soc. Chem. Ind., **15**, 90, 1896; Gill, ibid., **26**, 185, 1907.

taken to replace any oil that is lost. The cotton is then placed in the cylinder, packed about the thermometer so that it occupies the upper 4½ in. of the cylinder, and put into the boiling water bath. After the expiration of an hour, the bath having been kept in active ebullition, the temperature is read. Any oil which shows a temperature exceeding 100° C. in one hour, or 200° C. in two hours, should be regarded as a dangerous oil, or liable to produce spontaneous combustion. The following tables show the results obtained in using this apparatus.

Oil.	Temperature °C. in		
	1 hr.	1½ hrs.	1¾ hrs.
Olive (neutral)	97–98	100	101
Cotton-seed	112–128	177–242	194–282
Elaine	98–103	101–115	102–191
Olive fatty acids	102–114	.....	196

Other values obtained were:

Oil.	Temp. °C.	Time Minutes.	Iodine, No.	Free Acid, per cent.
Olive	234	130	85.4	5.3
Lard	234	75	75.2	Trace
Oleic acid	158	188	60.5	.....
Cotton-seed	234	70	108.9	Neutral
Linseed	234	65	168.1	Neutral
25° Paraffin	97	135	16.2	.....

Besides being used for testing oils it can be applied to testing other materials, oily waste, sawdust, or any mixtures suspected of causing spontaneous combustion.

"The results [1] of the greatest practical value obtained in the use of this apparatus have been, first, determining the cause of fires; and, second, determining the degree of safety of the various oils used in manufacturing. Mineral oil, as is well known, is not liable to spontaneous combustion; and a certain percentage of animal or vegetable oil may be added to mineral oil without materially increasing the danger under ordinary circumstances. This percentage varies according to the oil; with neat's-foot and first quality lard oil some 50 to 60% may be used, with cotton-seed not over 25% is allowable. The claim so often made for so-called 'safe' oils, said to have been changed by special and secret processes of refining so as to be no longer dangerous, is easily exposed by this test."

Drying Test Upon Glass.[2] A few drops of oil are brought upon a glass plate inclined at about 30° from the horizontal. A test of the oil is made from time to time by touching it with the fingers, the time at which it does not soil them being noted as the point when it is dry. Good oil should dry in three days.

Archbutt [3] makes this test as follows: A piece of polished plate-glass 7 cm. square by 4 mm. thick is cleaned and counterpoised on the balance; it is then heated for an hour at 200° C. in an air bath to thoroughly dry it. It is taken out,

[1] Richards, Tech. Quarterly, 4, 346, 1891.
[2] Amsel, J. Soc. Chem. Ind., 15, 222, 1896.
[3] J. Soc. Chem. Ind., 18, 347, 1899.

laid on a non-conductor, allowed to cool for three or four minutes, and the hot glass thinly painted with the oil to be tested by means of a camel's-hair brush. When the glass is cold it is weighed and sufficient oil added to make it up to 0.1 gram. Two glasses are coated with the sample and two with a standard oil, all placed on a level surface in a large air bath at 50° C. and heated for nine hours; one set of plates is withdrawn, cooled, and tested by the finger. Good raw linseed is tacky, when tested by the finger when cold, in nine hours and dry in twelve; corn oil is practically dry in fifteen hours, though slightly tacky; cottonseed, partially dry in eighteen hours and fully dry in twenty-one. Refined rape oil dried in forty-eight hours, and olive oil was sticky after thirteen days.

Titer Test. Under this rather misleading title is expressed the solidification point of the fatty acids derived from a fat or oil; it has nothing at all to do with titration, as might be expected. The test is extensively used for the evaluation of fats, and according to the method provisionally adopted by the Association of Official Agricultural Chemists is carried out as follows:[1]

(*a*) *Standard Thermometer.* The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about 15 in. over all. The thermometer is annealed for 75 hours at 450° C., and the bulb is of Jena normal 16''' glass, moderately thin, so that the thermometer will be quick acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear-cut and distinct, but quite fine.

(*b*) *Determination.* Saponify 75 grams of fat in a metal dish with 60 cc. of 30% sodium hydroxide (26° Baumé) and 75 cc. of 95% (by volume) alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30% sulphuric acid (25° Baumé) to free the fatty acids, and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using the hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15 or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 in.) and made of glass about 1 mm. in thickness. Place in a 16-oz. salt-mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 by 6 in.), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.1° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

[1] U. S. Dept of Agriculture, Bureau of Chemistry Bulletin No. 107, p. 135, 1907.

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95% by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp.gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

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EDIBLE FATS

These include butter, lard and hardened oils.

Butter is examined for water, fat, ash, curd, and salt; these are usually present in the following proportions:

	Per cent.	Average per cent
Fat	78. -90	82
Water	5. -20	12
Salt	0.4–15	5
Curd	0.1- 5	1

These are determined as follows: weigh about 2 grams of butter into a platinum Gooch crucible half filled with ignited fibrous asbestos, and dry it at 100° C. to constant weight. The loss is the amount of ***water***. Dissolve out the fat by repeated treatment with petroleum ether and again dry to constant weight. The loss represents the amount of ***fat***. Ignite the crucible with a low flame or in a muffle, being careful not to volatilize the salt, until a light-gray ash is obtained. The loss represents ***curd*** and the residue ***ash***. By extraction of the ash with water, and neutralization with calcium carbonate, the salt can be titrated with silver nitrate.

Examination of the Fat. Butter is adulterated with oleomargarine, renovated butter, and cocoanut oil. The first may be detected by testing for cottonseed or sesamé oil either by the color tests or by the index of refraction; this at 25° is for butter 1.459–1.462, for oleo. 1.465–1.470. Owing to the fact that butter contains a large per cent of volatile fatty acids (butyric, caproic, caprylic and capric acids, in all about 8%), adulterants may be detected by determining the amount of these. The process usually employed is that of Reichert modified by Meissl.

Five grams of the clear fat, filtered through absorbent cotton, are weighed into a 250-cc. round-bottomed flask and saponified by 2 cc. potassium hydroxide 1 : 1 and 10 cc. of 95% alcohol, under a return flow condenser for twenty-five minutes. The alcohol is rapidly evaporated off on the water bath until no odor of alcohol is perceptible. Add slowly 160 cc. of recently boiled distilled water which has been cooled to 50° or 60°; warm the flask until a clear solution of the soap is obtained. Cool to about 60° and add 8 cc. sulphuric acid 1 : 4 to liberate the fatty acids. Drop into the flask two bits of pumice (about the size of peas) which have been

heated and quenched in water, and tie in a well-fitting cork; warm the flask until the fatty acids have melted and are floating on the liquid. Cool to about 60° and attach the flask to a condenser, using a trap to prevent the sulphuric acid from being mechanically carried over; 110 cc. are distilled into a graduated flask in as nearly thirty minutes as possible. Thoroughly mix the distillate, pour through a dry filter, and titrate 100 cc. with N/10 NaOH, using phenolphthalein as an indicator. Multiply the cc. of alkali by 1.1 and calculate them to 5 grams of fat. The Reichert-Meissl value for butter is from 24 to 34, the average is about 28.8; cocoanut oil gives 6–8 and other fats less than 1.

The procedure is a conventional one and should be followed as exactly as possible. Cocoanut and other vegetable oils would be shown by the fact that the unsaponifiable matter would contain phytosterol; also by the Polenske number.[1] Renovated butter is best shown by the "Spoon or Foam Test." This consists in melting a third of a teaspoonful of the sample in a tablespoon over a small flame and stirring with a match. Increase the heat until the fat boils briskly, stirring thoroughly several times. Oleomargarine and renovated butter boil noisily, sputtering like a mixture of grease and water and produce no foam. Butter boils with less noise and much foam sometimes rising over the sides of the spoon. The pieces of curd in butter are much smaller than in either of the others.

Preservatives. benzoic, boric and salicylic acids, may be examined according to the procedure given in Woodman and Norton, "Air, Water and Food," pp. 154 and 196.

Color may be detected according to Allen, "Commercial Organic Analysis," 4th Ed., Vol. II, or Leach's "Food Analysis."

Lard is adulterated with water, 25% being added in some cases, with cottonseed oil or stearine and beef stearine.

Water is determined as with butter; ***cottonseed oil*** or stearine by the usual tests. It should be borne in mind, however, that hogs fed on cottonseed meal yield a lard which will give the Halphen test as strongly as if it contained 25% of the oil. The iodine number and the presence of phytosterol will confirm this test; the iodine number varies widely according to the source of the fat, but in general it may be said it should be between 46 and 66.

Beef stearine is very difficult if not impossible of detection. For this, reference may be had to Lewkowitsch, 5th Ed., Vol. II.

HARDENED OILS

As the name denotes, these are oils which have been changed to more or less solid fats by the addition of hydrogen, in the presence of a catalyst, usually a compound of nickel. This betrays their presence and may be tested for as follows:[2]

Ten grams of the fat are heated on the water bath with 10 cc. of hydrochloric acid (sp. gr. 1.12) with frequent shaking for two or three hours. The fat is removed by filtering through a wet filter, receiving the filtrate in a porcelain dish; after partial evaporation of the filtrate 2 or 3 cc. of strong nitric acid are added and the evaporation continued to dryness to ensure the destruction of the organic matter. The residue is dissolved in a few cc. of distilled water, a few drops of a

[1] Z. Nahr. Genussm., 7, 193, 1904, also Leach, "Food Analysis."
[2] Kerr, J. Ind. and Eng. Chem., 6, 207, 1914.

1% solution of dimethyl glyoxime in alcohol added, and a few drops of dilute ammonia. The presence of nickel is shown by the appearance of the red-colored nickel dimethyl glyoxime. The amount of nickel can be determined colorimetrically by comparison with solutions containing known quantities.

The quantity of nickel is very minute, not as much as the fats take up when cooked in nickel or nickeled dishes and need cause no apprehension.

Hydrogenation destroys all the characteristics, particularly the color tests, by which the different oils may be sometimes detected.

WAXES

These, as will be remembered, contain no glycerine; the tests applied to them are the same as to the oils. The characteristics of the more commonly occurring waxes are given in the table, p. 606; sperm oil, which is really a liquid wax, is included among the oils.

MISCELLANEOUS OILS AND LUBRICANTS

PROPERTIES OF SOME OF THE MINERAL OILS

Oil.	Specific gravity, deg. Baumé at 60° F.	Flash point, °F.	Viscosity (Saybolt), at 70° F.	Cold test, deg. Fahr.
Black	29	325	100–120	5–15
Ice machine	26–27	325–360	60–100	0–4
Crank case	26–27	455	100	
Transformer	.....	340–380	400	25
Turbine	30	420	160	.....
Spindle	30–35	320–390	58–156	.....
Loom	28	360	203	.....
Engine	27–30	410	190–210	.....
Cylinder	23–25	525	200–300*	.....
Cylinder	26–28	400–575	.....	.....

* At 212° F.

Belt Dressings are (1) mixtures of fats, waxes, degras or tallow with castor or fatty oils; (2) vulcanized corn or cottonseed oil thinned with naphtha; (3) preparations containing wood tar; or (4) preparations containing rosin, which is undesirable. Black oils, car oils, well oil or reduced oils are crude oils from which the naphthas and burning oils have been separated by distillation. Crank-case oils are pure mineral oils which emulsify but little with water. Milling-machine or soluble oils are lard, sulphonated oils or mineral oils held in suspension in water by soaps or alkalies, as borax or soda; the soaps used are either ammonium, sodium or potassium with resin, oleic or sulphofatty acids. Rosin oils are obtained by distilling or "running" rosin, each distillate being called a "run" and numbered according to the times it has been distilled. They oxidize quite rapidly and should not be used as lubricants except as soaps in lubricating greases. Screw-cutting oils are often mixtures of 27° Bé. paraffin and 25% fatty oil, preferably cottonseed, although lard oil was formerly used. Stainless oils are spindle or loom oils mixed with fatty oils—lard or neatsfoot. Transformer oils should be either pure mineral or rosin oils and as free as possible from water,

acid, alkali and sulphur. Turbine oils should be of excellent quality, free from acid and tendency to resinify, and low in sulphur. Watch oil is obtained from the porpoise, dolphin, or blackfish, where it exists in cavities in the jaw and in the brain or " melon " of the fish. Lubricating greases are mixtures of soaps of palm oil, tallow or rosin oil (with lime or soda as bases) with various oils or fats such as rosin, tallow or mineral oil. The best are those made from tallow by saponification with caustic soda. They may also contain finely powdered talc or graphite. Non-fluid oils are oils or their greases stiffened with " oil pulp " or "dope," i.e., aluminum oleate or palmitate.

The source, preparation and uses of the various oils and greases are described in Rogers and Aubert's Industrial Chemistry, Chapters XXII, XXIV, XXV and XXVII.

For the guidance of the analyst, the characteristics of the more frequently occurring oils are given, the usual figures being given in italic.

The vegetable oils may be classified into

Drying. Linseed, Chinese wood, poppyseed, sunflower and menhaden.

Semi-drying. Corn, cottonseed, sesamé, rape, black mustard and horse.

Non-drying. Castor, almond, peanut, olive, cocoanut, palm, seal, cod-liver, elaine, lard, neatsfoot, tallow, sperm and whale.

CHARACTERISTICS OF THE FATTY ACIDS FROM SOME OILS

Oil.	Refr. Ind. at 60° C.	M.pt. °C.	Solidifn. Pt. °C.	Iodine Per cent.
Almond	1.4461	13–14	9–11.8	93.5–96.5
Castor	1.4546	13	3	86–88
Chinese wood	—	40–43.8	31.2	145–159.4
Cocoanut	1.4295	24–27	15–20	8.4–9
Codliver, Medicinal	—	—	17–18 (titer)	164–171
Corn	—	18–21.6	14–16	113–125
Cottonseed	1.446	34–40	32–35	105–112
Elaine				
Horse		37.5–39.5	33.6–37.7	84–87
Lard		35		
Linseed	1.4546	17–24	13–17	179 209.8
Menhaden	No figures av	ailable.		
Black Mustard	1.4665 at 20°	9–17	6–8	108–126.5
Neatsfoot	—	28.5–29.8	16–26.5 (titer)	62–77
Olive	1.4410	19–31	17–24.6	86–90
Palm	—	47.7–50	36–46 44	53.3
Peanut	1.4461	27–35	22–32.5	95–103
Poppyseed	1.4506	20–21	16.5	139
Rape	1.4491	16–22	16–18	99–105
Seal	—	14–33	13–17	186–202
Sesamé	1.4461	23–32	18–26	109–112
Sperm	—	13–21	16	83–99
Sunflower	1.4531	17–24	17–18	124
Tallow				
Whale	—	14–27	23–24	130–132

CHARACTERISTICS OF SOME OILS

Oil.	Sp.Gr. 15° C.	Refr. Ind. 15° C.	Valenta °C.	Elaidin.	Maumené °C.	Sap. No. mg.	Iodine %	Composition.	Common Adulterants.	Visc. U. Sec. 100° F.	Flash °F.[1]
Almond	0.914–.920 *.918*	*1.4738*	*110*	Solid	53	190–195.4	93–101 *97*	Olein, linoleim.	Peach and apricot kernel, cottonseed, peanut, lard, olive, sesamé and poppyseed.		
Castor	0.959–.968	1.4795–.4803	Soluble	Solid	46–47	176–186	81–90	Ricinolein, stearin, dihydroxy stearin.	Blown oils, linseed, rape, cottonseed and rosin.	1485	505
Chinese wood or tung oil	0.940–.944	1.503 at 19°	40–47	Liquid and solid	—	190–197	156–176	Olein, elacomargarin.			
Cocoanut	0.926 0.874 at 99° C.	1.4573	—	—	—	225–268	8–10	Caproin, caprylin, caprin, olein, laurin, myristicin, palmitin, stearin.	Rarely adulterated.		
Codliver, medicinal	0.922–.941	1.478–1.481	—	Liquid and solid	100–116	183–188	135–198	Palmitin, stearin, jecolein, therapin	Salmon, seal, whale, shark liver; oils from other Gadidæ are not, commercially speaking adulterants.		
Corn or maize	0.921–.927 *.922*	1.4768	80	Pasty	56–88 *85*	189–193 *191*	111–123 *115*	Palmitin, arachidin, olein, linolein.	Rarely adulterated.	187	480
Cottonseed	0.921–.930 *.922*	1.4737–4757	90–110	Pasty	70–90 *76*	191–196	101–117 *108*	Stearin, palmitin, olein, linolin, arachidin.	Rarely adulterated.		
Elaine or Red	0.899–.908	1.4631 at 25° C.	—	Solid	—	200	90	Oleic, palmitic and stearic acids.	Cottonseed and mineral.		
Horse	0.916–.922	1.4652–.4704	54–80	—	46–55	195–197	75–86	Similar to lard but dries.	Rarely adulterated.		
Lard	0.914–.916	1.4694	54–98	Very solid	39–47 *43*	190–196	60–88	Olein, stearin, palmitin.	Cottonseed, tallow, corn and mineral.	214	565
Linseed	0.9315–.9371 *0.932–.936*	1.4835	57–79	Liquid and solid portion	103–126 *90*	187–195.2 *189–194*	167.6–205.4 *178–190*	Isolinolein, linolein, linolin, olein, stearin, palmitin.	Corn, cottonseed, fish and rosin.		
Maize	See Corn										

[1] With covered tester.

Menhaden	0.927–.936 *0.930*	1.4783	64	As linseed	123–128 *126*	189–193 *190*	139–193 *154*	Linolein, myristin, asellin, and acetin, clupanodonin.	Mineral and rosin.		
Bl'k Mustard	0.917–.919	1.4672	Insoluble	Pasty	42–43	173–176	98–110	Like rapeseed.	Sesamé.		
Neatsfoot	0.915–.916	1.4695–.4705	62–75	Solid at times	42–49.5	194–199	66–76	Olein, palmitin and stearin.	Other hoof oils, fish, poppy seed, rape, cotton-seed and mineral oils.	224	440
Olive	0.915–.920 *.916*	1.4703–.4713	85–111	Very Solid	35–47 *41*	185–203 *190*	77–94 *82*	Olein, palmitin, arachidin and linolin.	Cottonseed, peanut, rape, sesamé, poppyseed and lard.		
Palm	0.920–.924 0.859 at 99° C.	1.451 at 60°	—	—	—	196–202	53–57	Palmitin, palmitic acid and stearin.	Water, sand and dirt.		
Peanut or Arachis	0.916–.925 *.917*	1.4731	87-112	Solid	46–75 *51*	185–197 *194*	83–105 *98*	Palmitin, linolin, olein, arachidin and lignocerin.	Cottonseed, rape, sesamé and poppyseed.		
Poppyseed	0.924–.927 *.925*	1.4773	—	Pasty	87	190–197 *193*	133–143 *138*	Linolin, linolein and isolinolein, olein, stearin, palmitin.	Sesamé.		
Rape or Colza	0.913–.917 *.916*	1.472–.4757	Insoluble	Pasty	49–64 *55*	168–178 *174*	94–106 *101*	Stearin, olein, erucin, rapin, and arachidin.	Cottonseed, poppyseed, hempseed, linseed, fish oil.	247	455
Seal	0.924–.933	1.477	—	Pasty	—	178–196 *188*	127–193 *147*	Palmitin, olein, hypogaein.	Mineral and rosin.	164	515
Sesamé	0.922–.924	1.4748–.4762	87–107	Pasty	63–72	187–194	103–115	Stearin, palmitin, olein and linolin	Cottonseed, peanut, rape and poppyseed		
Sperm	0.844–.880 .884	1.4664–.4673	Insoluble	Solid at times	45–51	123–147	70–96	Contains no glycerin, palmitic acid.	Whale, mineral, rape, liver and arctic sperm.	115	455
Sunflower	0.924–.926	1.4762	—	Pasty	72–75	188–194	119–133	Linolin, olein.			
Tallow	0.916	1.4660 at 25° C.	71–75	Solid	35	197	56	Similar to lard.			
Turpentine	See page 617.										
Whale	.917–.927	1.4691 at 25°	—	Pasty	88	188–193	110–136	Palmitin.	Seal oil.	184	515

CHARACTERISTICS OF SOME WAXES

Wax.	Sp.Gr 15° C.	Ref. Index at 40°	M.pt.	Solid Pt.	Sapn. Value.	Acid Value.	Iodine Value.	Composition.	Common Adulterants.
Carnauba	0.99-.999	65-69°	83-91	80-87	79-88	0.3-7.0	5-13.2.	Ceryl and myricyl cerotate, carnaubate and a hydrocarbon.	Stearic acid, ceresin and paraffin.
Candelilla	0.969-.993	At 71.5° 1.455	65-68	63-68	46-65	10-21	14-36.8	Hydrocarbon, myricyl alcohol	Like carnauba wax.
Beeswax	0.959-.970	At 75° 1.439-1.445	62-70	60-63	87-107	16.8-21	7.9-11	Cerotic and melissic acids, myricin, ceryl and myricyl, alcohols, hydrocarbons.	Water, mineral matter, flour, starch, tallow, stearic acid, other waxes, rosin.
Chinese or Insect	0.970	—	80-81	80-83	80-93	51% fatty acids	1.4	Ceryl cerotate.	
Spermaceti	0.905-.960	—	41-46	41-47	120-134.6	49-53% fatty acids	3.8	Cetyl palmitate.	Stearic acid, beeswax, tallow, paraffin.
Woolfat or wax	0.941-.97	—	Acids 31-42	Acids 40	82-130	—	15-29	Ceryl and carnaubyl alcohols, cholesterol, lanoceric, lanopalmic, myristic, and carnaubic acids.	
These two below are really fats but are called waxes.									
Japan	0.975	—	50-51	48-50.8	217-237.5	—	4.2-15.1	Palmitin and palmitic acid.	Water, starch, other fats.
Myrtle	0.995	At 80° 1.436	40-48	39-45	205-217	—	1.9-3.9	Palmitin.	

MULTIPLYING FACTORS TO REDUCE SAYBOLT TIMES TO ENGLER NUMBERS OR TO REDWOOD TIMES [1]

Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Saybolt Time to Redwood Time.	Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Saybolt Time to Redwood Time.
28	0.0357	0.95	75	0.0289	0.86
30	.0352	.95	80	.0286	.86
32	.0346	.94	85	.0284	.86
34	.0342	.94	90	.0282	.85
36	.0337	.94	95	.0280	.85
38	.0334	.93	100	.0279	.85
40	.0330	.93	110	.0276	.85
42	.0327	.92	120	.0274	.84
44	.0323	.92	130	.0272	.84
46	.0320	.91	140	.0271	.84
48	.0317	.91	160	.0269	.84
50	.0314	.90	180	.0268	.84
55	.0308	.90	200	.0267	.84
60	.0302	.89	....	.....	....
65	.0297	.88	1800	0.0267	0.84
70	0.0293	0.87			

The Engler number is the quotient of Engler Time divided by the water value of the instrument at 20° C. in seconds.

Reagents

The reagents used in oil analysis are few and easily obtained. A list and their method of preparation is here given.

Acetic Acid, Glacial. Baker and Adamson's C. P. or Kahlbaum's "Eisessig," 99.5 % pure. The determination of its strength should be made by titration and not by specific gravity, as the 98% and 80% acid have the same specific gravity, 1.067. The determination of the melting-point gives results equally good with those obtained by titration and requires less time.[2] It is made after the manner of the "titer test" (p. 598), the tube being half filled, chilled to 10 to 11° C., and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting-point, where it remains stationary for some time. The melting-points of acids of various strengths are as follows:

100%, 16.75° C.; 99.5%, 15.65°; 99%, 14.8°.

For Hanus's solution it must not reduce potassium bichromate and sulphuric acid.

Acetic Anhydride. Baker and Adamson's C. P. or Kahlbaum's "Essigsäures Anhydrid."

Alcohol. Commercial "Cologne Spirits." For the preparation of alcohol free from aldehyde for alcoholic potash, cologne spirits are treated with silver oxide as follows: 1½ grams of silver nitrate are dissolved in 3 cc. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 cc. warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled, a few bits of pumice, prepared by igniting it and immediately quenching under water, being added to prevent bumping. Alcohol for use in the free acid determination is prepared by placing 10 to 15 grams of dry sodium carbonate in the reagent bottle, taking care to filter it before use.

Alcohol, Amyl. Kahlbaum's manufacture.

Bromine. The commercial article; also a N/3 solution, made by dissolving 26.6 grams bromine in 1 liter carbon tetrachloride.

[1] Proc. Am. Soc. Test. Mat., **15**, 1, 288, 1915.

[2] McIlhiney et al., J. Am. Chem. Soc., **29**, 1224, 1907.

Calcium Chloride. The dry and also the crystallized salt.
Calcium Sulphate. Plaster of Paris.
Carbon Tetrachloride. Baker and Adamson's C. P. or Kahlbaum's "Tetrachlorkohlenstoff."
Chloroform. Squibb's, U. S. P.
Copper. Copper turnings or clippings, used for the generation of nitric oxide.
Copper Wire. Cut in pieces of 0.3 to 0.5 gram.
Ether. Squibb's, U. S. P.
Gasoline. Gasoline, 86° Baumé.
Hydrochloric Acid, C. P.—Specific gravity 1.2. For N/2 HCl dilute 39 cc. of the above acid to 1 liter and standardize.
Iodine Solution. Fifty grams of iodine to 1 liter of alcohol. For Hanus's solution dissolve by warming 13.2 grams iodine in 1 liter glacial acetic acid; cool and add 3 cc. of bromine.
Lead Acetate. One hundred grams of the salt to 1 liter.
Lacmoid. Three grams per liter of dilute alcohol.
Lacmoid Paper. Unsized paper dipped in above solution.
Litmus Paper.
Mercuric Chloride. Sixty grams of the salt to 1 liter of alcohol.
Nitric Acid. Specific gravity 1.34.
Phenolphthalein. One gram of the substance to 500 cc. of alcohol.
Meta-Phosphoric Acid. A saturated solution of the commercial "stick phosphoric acid" in absolute alcohol.
Potassium Bichromate. Dissolve 3.8633 grams of the C. P. salt in 1 liter of water; 1 cc. is equivalent to 0.01 gram of iodine. The solution should be tested against iron wire containing a known percentage of iron.
Potassium Hydrate. N/2: Dissolve 30 grams of "potash by alcohol" in 1 liter of alcohol. N/6: Dissolve 10 grams of "potash by alcohol" in 1 liter of water and dilute to proper strength. The solution should be protected by "stick potash" from the carbon dioxide in the air. *Ten per cent.:* Dissolve 100 grams of "stick potash" in 1100 cc. of alcohol.
Potassium Iodate. A 2% solution.
Potassium Iodide. One hundred grams of the commercial salt are dissolved in 1 liter of water. This should be free from iodate, shown by yielding no coloration when acidified with strong HCl.
Silver Nitrate. Thirty grams to 1 liter+0.4 cc. HNO_3.
Sodium.
Sodium Chloride. Ordinary "coarse fine" salt for freezing mixtures.
Sodium Hydrate. 36° Baumé. Dissolve 300 grams of caustic soda in 1 liter of water.
Sodium Nitroprusside. The commercial salt.
Sodium Thiosulphate. N/10: Dissolve 26 grams of "sodium hyposulphite" in 1 liter of water. See page 204.
Starch Solution. Rub up in a mortar 1 gram of potato starch, with 10 to 15 cc. of water, pour this into 200 cc. of water which is boiling actively, and continue the boiling for a few minutes.
Sugar. Ordinarily granulated sugar.
Sulphur. A 1.5% solution in carbon bisulphide.
Sulphuric Acid. C. P. This should be at least 99.5% pure, and its strength be determined by titration, as 100% and 94.3% acid have the same specific gravity.
Dilute. One part acid to ten parts water.
Nitrosulphuric Acid, for the Elaidin Test. A liter of sulphuric acid of 46° Baumé (1.47 specific gravity) is prepared by diluting 560 cc. commercial sulphuric acid to 1 liter; a few drops of nitric acid are added and nitric oxide (generated from copper and nitric acid) passed in until it is saturated. The acid is then cooled in ice-water and the gas passed in until it is saturated at 0° C. This is called Roth's liquid.

The author wishes to acknowledge his indebtedness to Mr. Thomas T. Gray for the careful review of this chapter. Mr. Gray's broad experience in petroleum products, as Chief Chemist of Tidewater Oil Company, makes his criticism especially valuable and of special value.

[1] Richmond, J. Soc. Chem. Ind., **9**, 479, 1890.

ANALYSIS OF PAINTS

HENRY A. GARDNER.[1] AND JOHN A. SCHAEFFER.[2]

In reporting the results of an examination of a paint, it is advisable to give all the analytical data as well as a résumé showing the probable composition of the paint. This is shown in the following example:

RESULTS OF ANALYSIS

Total Pigments or Solids	60%
Total Vehicle or Liquids	40

Analysis of Pigment Portion

Lead Oxide (PbO)	37.47%
Zinc Oxide (ZnO)	44.50
Alumina, iron, lime	2.90
Magnesia (MgO)	1.90
Silica (SiO_2)	4.63
Carbon Dioxide (CO_2)	2.50
Sulphuric Anhydride (SO_3)	5.02
Water (combined)	.73
	99.15%

Analysis of Vehicle Portion

Vehicle contained 20% volatile matter.
Volatile matter consisted of equal parts of turpentine and mineral spirits.
Non-volatile matter had:

Iodine Number	175
Acid Number	2.4
Saponification Number	188

and contained .02% ash consisting of lead and manganese oxides.

Probable Composition of Paint.

Pigment	60%
Liquid	40

Pigment

Basic Carbonate—White Lead	22%
Basic Sulphate—White Lead	25
Zinc Oxide	43
Asbestine	10
	100%

Liquid

Raw Linseed Oil	80%
Mineral Spirits	10
Turpentine and Drier	10
	100%

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[2] Chief Chemist, Pilcher Lead Co., Joplin, Mo.

ANALYSIS OF PAINT VEHICLES

Composition of Liquid Part. The vehicle or liquid portion of paints may contain various fixed animal, vegetable or mineral oils, oleo-resinous varnishes, turpentine, mineral distillates, benzol and driers.

It is always advisable to determine the total percentage of liquids in a paint. The container should be thoroughly shaken so that the contents will be uniform throughout. A portion of 4 or 5 ounces may then be removed and placed in a screw-cap bottle. The original can of paint should then be set aside so that settling of the pigments will take place. Unless the paint is in paste form, this will usually be accomplished in twenty-four hours. A portion of the clear liquid floating over the pigments may then be removed and directly examined as outlined under Separation of Vehicle Components.

Percentage of Liquid by Ignition Method. The percentage of vehicle in the uniform sample of paint previously obtained may be found by placing a weighed portion in a porcelain crucible and slowly igniting it to burn off the organic constituents. By carefully regulating the heat, the oil and volatile thinners will be slowly burned off, leaving the pigment behind, which may then be weighed, calculating the vehicle by difference. This method is a rapid one and works well with some pigments. When pigments are present which show an appreciable loss on ignition, or blacks or blues, this method is not to be relied upon.

Percentage of Liquid by Extraction Methods. Another good method of separating the vehicle from a paint is to place a portion in a large tube, adding a considerable quantity of benzol, petroleum ether, or that portion of gasoline distilling below 120° C., subsequently centrifuging. Pigments which settle slowly are thrown down very rapidly by this method. The process is repeated three or four times in order thoroughly to free the pigment from oil. After drying, the pigment is weighed and the percentage of vehicle determined by difference. In case a centrifuge is not available, the vehicle of many paints may be separated by simply shaking a portion of the paint in a long test-tube with benzol, allowing the pigment to settle, repeating the extraction until the oil is thoroughly removed.

Some operators have from time to time used a Soxhlet extractor for the determination of the vehicle of a paint. This method is rather slow and does not always give satisfactory results.

It must be remembered that no method of extraction of the oil from a paint will give absolute results. The last traces of oil cannot be removed from the pigment, which is probably due to the fact that many pigments such as lead and zinc react with the oil, producing small quantities of insoluble soaps which are not completely dissolved by the solvent.

In the extraction of paints, the choice of a solvent is important. When benzol (90°) is not available, it may be replaced by gasoline that has been redistilled, using the light fraction coming over below 120° C. This cannot be used, however, when varnish resins other than rosin are present, as they are insoluble therein.

There are some pigments which by reason of their low specific gravity, colloidal nature or partial solubility can never be completely separated from oil, either by settling, centrifuging or extraction. Of these the most commonly met with are lampblack and other forms of carbon, zinc oxide and Prussian blue. Colloidal pigments such as zinc oxide are very troublesome in this respect. When these pigments, however, are present in a paint in considerable percentage, the

fficulty of their separation may be avoided by adding to the paint three or four nes its volume of fuller's earth, diluting the mixture in a large test-tube with soline or petroleum ether and either centrifuging or placing in a rack to settle. he fuller's earth carries down the colloidal pigments and the separation is sharp id easy. This method, of course, is simply used to extract the vehicle present. he pigment resulting from the separation cannot be used for analysis on account admixture with the fuller's earth.

In some cases the pigments in paste colors made of lampblack and Prussian lue cannot be separated from the vehicle portion. The amount of Prussian blue resent, however, may be determined by making a Kjeldahl-Gunning determina- on on a portion of the entire paint, multiplying the nitrogen found by 4.4. For ne determination of the lampblack present, a portion of the entire paint may be oiled with an excess of alcoholic potash until all of the oil is saponified. The ixture is then decanted through a filter and washed, first with hot alcohol and hen with hot water. This affords a very good separation of the vehicle from the igment of such paints. By this method, the Prussian blue which may be present s partially destroyed, the iron content remaining admixed with the black pig- nent on the filter.

Separation of Vehicle Components. Whenever possible, it is advisable to letermine the constituents of the vehicle upon that sample that has been removed rom the top of the settled can of paint. A weighed portion of this vehicle may be placed in a tared flask and attached to a Liebig condenser. Heating to 180° C. or lower will drive off nearly all the volatile constituents. The composition of the distillate may be determined by the methods given under the Examination of Turpentine. A portion of the residue in the flask, which consists of oil, driers, gums, etc., may be transferred to a crucible and ignited. The residue may then be weighed and calculated to ash. The ash should be analyzed for lead, manganese and other driers.

Another portion of the original vehicle may be evaporated in an atmosphere of CO_2 (prevents oxidation) to remove the volatile constituents. A portion of the oil residue may then be examined for iodine number and other constants. In some instances it would be advisable to make a saponification and extraction of the fatty acids from this residue, determining the iodine number on the fatty acids.

Water. For a direct determination of the percentage of water in a paint, the analyst may place a weighed quantity (approximately 100 grams) of the paint in a metal still, mixing it with an equal quantity of sand. Distillation will drive off the water and other volatile constituents which will separate into two layers in the graduate.

Direct Distillation for Volatiles. For a direct determination of the volatile constituents in a paint, a sample may be distilled *in vacuo*. This is easily managed wherever a vacuum pump is available and avoids the necessity of overheating the oil. When distilling by this method, a sample of the clear vehicle from a settled paint, in order to obtain the fixed oils for analysis, it should not be heated above 150° C. and neither should the solvent be volatilized in such a way as to allow the oil to be in contact with air, as it will oxidize rapidly while warm and its iodine number be very much lowered. The volatile may also be separated by steam distillation.

Detection of Resinates. To determine whether the drier in a paint is of the resinate type or linoleate type, a few drops of the oil vehicle may be mixed on a porcelain plate with one or two drops of acetic anhydride, subsequently adding a

drop of sulphuric acid. Upon the addition of the sulphuric acid, a flash of purple color, turning to dark brown, will be shown where rosin is present. If rosin should be present in the vehicle to a considerable extent, the oil will have a very high acid number. The approximate percentage of rosin present may be determined by shaking a portion of the vehicle with 95% alcohol in a separatory funnel, subsequently separating the alcoholic extract, evaporating and weighing the residue.

Detection of Various Oils. Chinese wood oil may be detected in the vehicle by mixing the oil with an equal volume of a saturated solution of iodine in petroleum ether, allowing the mixture to stand in direct sunlight. Under these conditions, a peculiar, insoluble, spongy polymer of one of the fatty acids of Chinese wood oil is shown. Fish oil can usually be detected by its odor and the dark red color during saponification. The presence of soya bean and other vegetable oils is in some cases difficult to detect. The iodine numbers of these oils, however, are all lower than that of linseed oil. It must be remembered, however, that the iodine number of boiled linseed oil is lower than that of raw oil and that the iodine number of oils extracted from many paints is usually lower than shown by the original oil. In the presence of considerable quantities of drier, it is always advisable to extract the fatty acids from oil and make the iodine determination upon them.

The distillate from the paint vehicle may consist of turpentine, mineral distillates, benzol and similar solvents. The presence of benzol is readily detected by adding a few drops of the distillate to a small quantity of a mixture of concentrated nitric and sulphuric acids. Upon heating this mixture, the characteristic odor of nitro-benzol will be recognized if benzol is present. Mineral distillates from petroleum are easily detected by the polymerization method given under the Examination of Turpentine.

ANALYSIS OF PAINT OILS

Although linseed oil is used to the greatest extent in paints, some other oils find use in the manufacture of special paints. The following have been used for this purpose: soya bean, perilla, corn, cottonseed, sunflower, lumbang, and similar vegetable oils; menhaden, herring, and similar marine animal oils of relatively high iodine number. All of the above named oils may be analyzed by applying the test for specific gravity, acid number, saponification number, unsaponifiable matter, and refractive index, as outlined for the analysis of Chinese wood oil. The iodine numbers of these oils are, however, better determined with Hanus solution, according to the following method:

Iodine Number. Weigh in a small glass capsule from 0.2 to 0.3 gram of oil, transfer to a 500-cc. bottle having a well-ground stopper, dissolve the oil in 10 cc. of chloroform and add 30 cc. of Hanus solution; let it stand with occasional shaking for one hour, add 10 cc. of a 10 per cent solution of potassium iodide and 150 cc. of water, and titrate with standard sodium thiosulphate, using starch as indicator. Blanks must be run each time. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 gram of oil). The iodine number of raw linseed oil varies from 175 to 193. Make the Hanus solution by dissolving 13.2 grams of iodine in 1000 cc. of glacial acetic acid which will not reduce chromic acid, and adding 3 cc. of bromine.

Analysis of Chinese Wood Oil (Tung Oil)

The analysis of Chinese wood oil requires the application of several tests not used for the examination of other oils. There is presented herewith a complete outline for determining not only the regular constants of oils, but the additional tests that have been adopted for the identification of pure tung oil. These tests constitute the recommended methods of Sub-Committee III of Committee D-1 of the American Society for Testing Materials, of which one of the writers is chairman.

Specific Gravity. Use a pyknometer accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making the test at 15°.5 C., water being 1 at 15°.5 C.

Acid Number. Weigh 10 grams of oil in a 200-cc. Erlenmeyer flask, add 50 cc. of neutral alcohol, connect with a reflux air condenser (or place small funnel in neck of flask), and heat on a steam bath for one-half hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with N/5 sodium hydroxide. Calculate as the acid number (milligrams of potassium hydroxide to 1 gram oil).

Saponification Number. Weigh from 2 to 3 grams of oil in a 200-cc. Erlenmeyer flask, add 30 cc. of a N/2 alcoholic solution of potassium hydroxide, connect with a reflux condenser, heat on a steam bath for one hour, then titrate with N/2 sulphuric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cc. of acid required by the blanks and the determinations, calculate the saponification number (milligrams of potassium hydroxide to 1 gram of oil).

Unsaponifiable Matter. To 25 grams of oil add 15 cc. of an aqueous solution of KOH (200 grams of KOH dissolved in water and made up to 300 cc.) and 35 cc. of 95% alcohol. Connect with a reflux condenser and heat on the water bath for one hour with occasional shaking. Transfer to a separatory funnel containing a little water and wash out flask with water, using in all 125 cc. Cool, add 200 cc. of ether and shake vigorously for one minute. In a few minutes the ether solution will separate perfectly clear. Draw off the soap solution into another separatory funnel. Shake the soap solution with three 100-cc. portions of ether. Unite all the ether portions and wash with three 30-cc. portions of water. Filter the ether solution (small portions at a time) into a tared flask, distill off the ether and dry flask and contents to constant weight at 95 to 100° C. in a steam oven. Report the percentage of unsaponifiable matter.

Refractive Index. Use a properly standardized Abbé refractometer at 25° C. or any other equally accurate instrument.

Iodine Number (Hübl). Place a small quantity of oil into a small weighing bottle or beaker. Weigh carefully. Transfer by dropping from 0.2 to 0.3 gram to a 500-cc. bottle having a well-ground stopper, or a specially flanged neck, iodine-test Erlenmeyer flask. Reweigh the weighing bottle or beaker to determine the amount of oil used in the test. Then dissolve the oil in 10 cc. of chloroform and add an amount of Hübl solution containing twice the amount of iodine that will be absorbed by the oil. Stopper the flask, shake well, and place in a dark closet for eighteen hours. Add 10 cc. of a 10% solution of potassium iodide and 100 cc. of distilled water. Titrate with N/10 sodium thiosulphate, using starch as an indicator. Blank tests must be made. From the difference between

the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 gram of oil).

On account of the fact that Hübl solution after preparation is apt to deteriorate in strength, it is considered advisable to have prepared the two component parts of Hübl solution, namely, a solution of mercuric chloride in alcohol and a solution of iodine in alcohol, of the proper strength, as outlined in text-books. The proper amounts of these solutions may be mixed on the day of use.

Heating Test (Browne's Method). Test-tubes for containing the oil should be 16 cm. by 15 mm., with a mark near the bottom to indicate 5 cc., and closed, by a cork so perforated that a glass rod 3 mm. in diameter can move freely.

Fill a copper beaker (height 12 cm.; internal diameter, 6 cm.) with cotton-seed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath.

Use a nitrogen-filled, immersed-stem chemical thermometer, engraved stem; total length 4 to 4½ ins.; graduated from 210 to 310° C. in 2° intervals; the length between 210 and 310° C. not less than 2½ ins. If preferred, use emergent-stem thermometer 30 cm. long, with graduations from 100 to 400° C., making correction for emergent stem according to the method outlined in Stem Correction Sheet No. 44 of the U. S. Bureau of Standards.

When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 cc. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time, remove the source of heat for about forty-five seconds and then reapply. Before two minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the wood oil has been in the bath about nine minutes, raise the glass rod at intervals of one-half minute, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds of fluidity, a good end-determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample.

No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the cotton-seed oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

Iodine Jelly Test. In a wide-necked 200-cc. Erlenmeyer flask, place 2.5 grams (weight correct to 1 milligram) of the oil. Add 10 cc. of chloroform from a pipette and stopper the flask immediately. Carefully insert a small glass vial into the flask so that the vial stands upright. Into the vial from a pipette run 10 cc. of a solution of iodine in chloroform, containing 0.035 to 0.036 gram of iodine per cc. Place the flask in a bath containing water at 25 to 26° C. and allow it to stand there for a few minutes. Keep the flask stoppered, except when it is necessary to remove stopper to insert the vial and to add the iodine solution. Tilt and rotate the flask so that the vial is upset and the contents of the flask are thoroughly mixed, at the same time starting a stop-watch. Keep the flask in the bath at 25 to 26° C. and at the end of every quarter minute tilt the flask towards a horizontal position. Note the time required for the formation of a jelly that does not flow, but sticks to the bottom of the flask or slides as a mass. Record time in minutes and quarters thereof. Pure Chinese wood oil should require 2¾ to 3¼ minutes for the formation of the jelly. If the temperature of the laboratory is more than 2 or 3° C. above or below 25° C., place the flask contain-

ing the iodine solution in the bath and allow it to remain there for several minutes before pipetting out the 10 cc. for the test.

A convenient procedure for preparing the iodine solution is as follows: Treat an excess of iodine with warm chloroform and after shaking for a few minutes cool the contents to about 20° C. and filter through glass wool. Pipette 10 cc. of the solution into a flask containing 10 cc. of 10% potassium-iodide solution and titrate with 0.1 normal sodium-thiosulphate solution. Calculate the iodine content and dilute with chloroform so as to obtain an iodine content of 0.035 to 0.036 gram per cc. After dilution, titrate again against the thiosulphate to be sure that the solution is of required strength.

All the details of the above method must be followed exactly.

The chloroform used to dissolve the oil and to prepare the iodine solution must conform to the requirements of the U. S. Pharmacopœia and must have a specific gravity at 25/25° C. of not more than 1.481 and not less than 1.480. The proper density can be obtained by washing with water if the specific gravity is too low, or by adding 95% ethyl alcohol if too high.

Standards for Chinese Wood Oil, A. S. T. M.

Raw Chinese wood oil should conform to the following requirements:

	Maximum.	Minimum.
Specific gravity at $\frac{15°.5}{15°.5}$ C.	0.943	0.939
Acid number	6	
Saponification number	195	190
Unsaponifiable matter, per cent	0.75	
Refractive index at 25° C.	1.520	1.515
Iodine number (Hübl eighteen hours)		165
Heating test (Browne's method), minutes	12	
Iodine jelly test, minutes	4	

Constants of Various Oils. The constants exhibited by some of the semi-drying and drying oils that have been used by one of the writers (Gardner) in making paints and paint tests are shown below. There are also given herewith the standards for raw and boil d linseed oil pressed from North American seed. Similar oils expressed from South American seed will generally show like constants, except for the iodine number, which will generally range from 170 to 180.

CONSTANTS OF VARIOUS OILS

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil	.931	183	188	2.0	1.4867
Soya Bean Oil	.924	129	189	2.3	1.4813
Menhaden Oil	.932	158	187	3.9	1.4850
Raw Tung Oil	.944	166	183	3.8	1.5050
Perilla Oil	.94	200	188	2.0	1.4874
Perilla Special	.94	192	189	3.2	1.4978
Heavy Bodied Linseed Oil	.968	133	189	2.8	1.4966
Lithographic Linseed Oil	.97	102	199	2.7	1.4978
Whale Oil	.924	148	191	9.2	1.4820
Boiled Linseed Oil (Linoleate Drier)	.941	172	187	2.7	1.4895
Corn Oil	.921	124.8	190.1	4.1	1.4800
Cottonseed Oil	.920	111.7	194.3	0.9	1.4781
Rosin Oil	.964	68.9	35.5	32.4	.....
Treated Tung Oil [1]	.882	56.4	101.3	7.7	1.4764
Lumbang Oil	.927	152	189	1.0	1.4789
Sunflower Oil	.924	124.6	189.3	7.5	1.4796
Hempseed Oil	.927	149.4	191.1	3.9	1.4822
Shark Oil	.910	132.8	158.9	5.2	1.4815
Sardine Oil	.919	134.6	177.3	10.4	1.4800
Petroleum Mixing Oil	.851	28.2	52.9	1.1	1.4773
Boiled Linseed Oil (Resinate Drier)	.936	184.2	187.6	7.3	1.4895
Peanut Oil	.932	102.2	188.0	2.2	1.4790

Boiled linseed oil from North American seed should conform to the following requirements, A. S. T. M.:

	Maximum.	Minimum.
Specific gravity at $\frac{15°.5}{15°.5}$ C	0.945	0.937
Acid number	8	
Saponification number	195	189
Unsaponifiable matter, per cent	1.5	
Refractive index at 25° C	1.484	1.479
Iodine number (Hanus)	.....	178
Ash, per cent	0.7	0.2
Manganese, per cent	.....	0.03
Calcium, per cent	0.3	
Lead, per cent	.....	0.1

Raw linseed oil from North American seed should conform to the following requirements, A. S. T. M.:

	Maximum.	Minimum.
Specific gravity at $\frac{15°.5}{15°.5}$ C	0.936	0.932
or		
Specific gravity at $\frac{25°}{25°}$ C	0.931	0.927
Acid number	6.00	.....
Saponifiation number	195	189
Unsaponifiable matter, per cent	1.50	.....
Refractive index at 25° C	1.4805	1.4790
Iodine number (Hanus)	.....	180

[1] Contained 30% volatile matter, largely high boiling-point petroleum spirits.

Examination of Turpentine

RECOMMENDED METHODS OF THE A. S. T. M.

Color. Fill a 200-mm., perfectly flat-bottom colorimetric tube graduated in millimeters to a depth of from 40 to 50 mm. with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter, place a No. 1 yellow Lovibond glass and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm. or more the turpentine is "Standard" or better.

Specific Gravity. Determine specific gravity at any convenient temperature with a plummet, the displacement of which has been accurately determined for that temperature, or by an equally accurate method, using the factor 0.00082 for each degree centigrade that the temperature of determination differs from 15°.5 C.

Refractive Index. Determine refractive index at any convenient temperature with an accurate instrument, and calculate the results to 15°.5 C., using the factor 0.00045 for each degree that the temperature of determination differs from 15°.5 C.

Distillation. Use an ordinary Engler flask and condenser,[1] and heat the flask by placing it in a glycerine or oil bath of the general type described in Bulletin No. 135, Bureau of Chemistry. Fit the flask with a thermometer reading from 145 to 200° C. in such a way that the mercury bulb shall be opposite the side tube of the flask and the 175° mark below the cork. Place 100 cc. of the turpentine to be examined in the flask, connect with the condenser, insert stopper bearing thermometer, and heat until distillation of the turpentine begins. Conduct the distillation so that the distillate passes over at the rate of 2 drops per second. Note the initial distilling temperature and the percentage distilling below 170° C.

Polymerization. Place 20 cc. of exactly 38/N (100.92 per cent[2]) sulphuric acid in a graduated, narrow-neck Babcock flask, stoppered, and place in ice-water and cool. Add slowly 5 cc. of the turpentine to be tested. Gradually mix the contents, cooling from time to time, and not allowing the temperature to rise above about 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the bottle in a water bath and heat from 60 to 65° C. for about ten minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking five or six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge at about 1200 R.P.M. from four to five minutes, or allow to stand for twelve hours. Read unpolymerized residue, notice its consistency and color, and determine its refractive index.

[1] Stillman, "Engineering Chemistry," p. 503.
[2] 4% free SO_3.

Standards for Turpentine, A. S. T. M.

Turpentine should be clear and free from suspended matter and water, and should conform to the following requirements:

The color shall be "Standard"[1] or better.

The specific gravity shall be not less than 0.862 nor more than 0.872 at 15°.5 C.

The refractive index at 15°.5 C. shall be not less than 1.468 nor more than 1.478.

The initial boiling-point shall be not less than 150 nor more than 160° C.

Ninety per cent of the turpentine shall distill below 170° C.

The polymerization residue shall not exceed 2% and its refractive index at 15°.5 C. shall not be less than 1.500.

ANALYSIS OF VARNISH

The testing of varnish should largely be of a physical nature. Such properties as odor, consistency, clarity, flowing, time of drying, character of finish, hardness, resistance to moisture and abrasion, elasticity, etc., point out the real value of a varnish. Chemical tests that give additional information, sometimes of a valuable nature, are as follows: Flash point, acid number, ash, character of solvent, fixed oil and resins.

Flash Point. A nickel or iron crucible of 60 mm. diameter and 40 mm. height is filled with the varnish to within 20 mm. of the top. It is then supported in a water bath in such a manner as to be about two-thirds immersed in the water. The water should be from 15° to 20° C. at the start and should be heated slowly so that the temperature of the varnish, as indicated by a thermometer suspended in it, will show a rise of about 1 degree per minute. Test for flash at each half degree, using a very small flame.

Acid Number. Ten to 20 grams of the varnish are weighed into a small Erlenmeyer flask, 50 cc. neutral alcohol added, and a small funnel inserted in the neck. Heat on the water bath for one-half hour, with occasional shaking. Allow to cool somewhat, add two drops of phenolphthalein indicator and titrate with tenth-normal potassium hydroxide solution. The acid number is the number of milligrams of KOH required to neutralize each gram of the varnish.

Ash. Weigh in a porcelain or fused silica crucible several grams of the varnish. Burn off over a small Bunsen flame, using great caution to avoid boiling over and spattering. When all combustible matter is destroyed, weigh the ash and if desired analyze it.

Solvent. Steam distillation of a portion of the varnish will remove the solvents, leaving a residue of fixed oils and varnish resins, which may be weighed after driving off the water. The distillate should be examined as recommended under Methods for the Examination of Turpentine. The amount of mineral spirits and turpentine may thus be determined.

Fixed Oils and Resins. In the above determination, the total amount of fixed oils and resins is obtained. It is a difficult matter, however, to determine the exact

[1] The term "Standard" refers to the color recognized as standard by the "Naval Stores Trade." Turpentine is of "Standard" color when a depth of 50 mm. in a perfectly flat polished bottom tube, approximately matches a No. 1 yellow Lovibond glass.

percentage and character of resins that have been used in the manufacture of the varnish. This is due to the fact that during the process of heating oils in the presence of resins many intricate chemical changes are brought about, a considerable portion of the resins being distilled off in the form of vapors and combinations of the oil brought about that are difficult of separation. One of the best methods, however, of separating the fixed oils and varnish resins is carried out in the following manner.

A portion of about a half ounce of the varnish resin should be placed in a 300-cc. tared beaker. There should then be added about 200 cc. of ice-cold petroleum ether and the beaker should be covered and allowed to stand, preferably in a dish containing ice. In an hour's time the resinous ingredients will be found precipitated at the bottom of the beaker or adhering to the side thereof (with the exception of rosin, which is largely soluble in petroleum ether). The precipitated resins should be washed with fresh portions of cold petroleum ether two or three times, pouring the decanted portions into a large bottle. The combined portions of petroleum ether may then be filtered through a tared filter, adding by the aid of a stirring rod the resins contained in the beaker. The filter paper and the beaker with the resins may then be dried at 100° C. and weighed. The combined filtrates may be distilled to obtain the fixed oil which may be examined for constants. (This fixed oil may contain rosin.) The amount of rosin contained in a varnish may be roughly ascertained by thoroughly shaking in a separatory funnel a portion of the varnish with a large quantity of absolute alcohol. The rosin may be obtained by evaporation of the alcoholic extracts. The fixed oils after oxidation or polymerization, as caused by the heating of the varnish during manufacture, are not readily soluble in alcohol.

Separation of Polymerized Oils and Resins. In the making of varnish, some oils become oxidized or polymerized to a condition resembling resins. For instance, when a varnish is examined for resins by the above method, it will often be found that a considerable amount of matter insoluble in petroleum ether will be obtained even when hard resins are absent. The insoluble substance is oxidized or polymerized oil. It may be differentiated from varnish resins by the fact that it is readily saponified by alcoholic potash. The following method by Boughton (Technologic Paper No. 65, U. S. Bureau of Standards), though involving considerable work, is probably the most accurate method for the separation of polymerized oils and resins.

To about 4 grams of varnish in a flask add about 25 cc. of water and boil until the volume is about 10 cc. This removes nearly all of the volatile. Add 25 cc. half normal alcoholic potash and 25 cc. benzol and boil under a reflux condenser for one-half hour. Evaporate the solution to about 15 cc. and add about 10 cc. of alcohol. Transfer completely to a separatory funnel, washing the flask with water and ether and using a policeman if necessary. Dilute with water to about 100 cc., add 100 cc. of ether, and shake. Add a few cc. of alcohol if necessary to make the layers separate. Draw off the aqueous layer and wash the ether three times with water and transfer to a tared flask for future use.

To the combined soap solution and washings, add an excess of hydrochloric acid and extract twice with 50 cc. of ether. Discard the aqueous layer, wash the combined ether extracts with water, transfer to a flask and distill off the ether. To the dry residue add 20 cc. of absolute alcohol and 20 cc. of a mixture of 1 volume of sulphuric acid and 4 volumes of absolute alcohol and boil for two minutes under a reflux condenser. Completely transfer the contents of the flask

to a separatory funnel, washing the flask with water and ether. Add 100 cc. ether and after agitation add 100 cc, of 10 per cent sodium chloride solution and again shake. Draw off the aqueous layer, extract it with 50 cc. of ether, combine the ether solutions and wash with water. Add 50 cc. of a fifth-normal potassium hydroxide solution and 10 cc. of alcohol, shake and draw off the lower layer into a second funnel. Wash the ether layer with 50 cc. of water containing 5 cc. of the potassium hydroxide solution and 5 cc. of alcohol.

Extract the combined aqueous portions with two 50 cc. portions of ether and finally wash the combined ether solutions (containing the ethyl esters of the fatty acids) with water.

Distill off the ether and boil the residue with 25 cc. of half-normal alcoholic potash for one-half hour under a reflux condenser. Transfer completely to a separatory funnel and extract the soap four times with ether. Wash the combined ether solution twice with water and add it to the first ether solution of unsaponifiable matter obtained.

Unite the solution and washings containing the soaps, add an excess of hydrochloric acid, and extract twice with ether. Transfer to a tared flask the combined ether solutions, after washing them with water, distill off the ether, dry the residue to constant weight at 110° C. and weigh as "fatty acids."

Report the percentage of fatty acids as percentage of oil and calculate the percentage of resin by difference.

OTHER MATERIALS

For detailed methods other than those given in this work, for the examination of shellac, resins, bitumens and other raw materials of the vehicle portion of paints and varnishes, the following references may be consulted:

Proceedings of the American Society for Testing Materials (Committee D-1), 1910–15.

Analysis of Paints and Varnishes. Gardner and Schaeffer. McGraw-Hill Book Co., New York.

Manufacture of Varnishes. Livache and McIntosh. Vols. I-III. Scott Greenwood & Son, London.

THE ANALYSIS OF PAINT PIGMENTS

The vehicle having been extracted from the paint under examination, by the previously outlined methods, the pigment is left ready for analysis. The pigment can be readily classified under one of the following heads by its color, thus shortening any preliminary examination. Many of the colors have a white base which necessitates a determination of both the colored portion of the pigment and any white base which may have been used.

The general analysis of colored pigments is carried out according to the specific method outlined for the individual colored pigments, together with the methods for a composite white paint, provided a qualitative examination does not directly reveal the identity of the pigment.

The pigments used in the manufacture of paints are classified as follows, in certain instances the trade names being given by which the particular pigments are known.

White Pigments

Lead Pigments

Sublimed White Lead—Basic Sulphate of Lead—Basic Sulphate—White Lead.
Corroded White Lead—Basic Carbonate of Lead.
Old Dutch Process White Lead.
Quick Process White Lead.
Mild Process White Lead.

Zinc Lead.
Leaded Zinc.

Zinc Pigments

Zinc Oxide—Zinc White.
Lithopone—Ponolith—Beckton White—Charlton White—Orr's White.

Silica Pigments

Silica—Silex.
Asbestine—Talcose.
China Clay—Kaolin—Tolamite.

Calcium Pigments

Whiting—Paris White—Chalk—Alba.Whiting—Spanish White.
Gypsum—Plaster of Paris—Terra Alba—Agalite.

Barium Pigments

Barytes—Barite—Blanc Fixe—Barium Sulphate.
Barium Carbonate—Witherite.

Red and Brown Pigments

Red Lead—Orange Mineral.
Vermilion.
Ochres—Tuscan Red—Indian Red—Venetian Red.
Umbers—Siennas.

Blue Pigments

Sublimed Blue Lead.
Ultramarine Blue.
Prussian Blue—Antwerp Blue—Chinese Blue.

Yellow and Orange Pigments

Chrome Yellow—Lemon Yellow—Medium Chrome Yellow.
American Vermilion—Orange Chrome—Basic Lead Chromate.
Orange Mineral.

Green Pigments

Chrome Green.
Chromium Oxide.
Green Earth.

Black Pigments

Graphite.
Carbon Black—Bone Black—Lamp Black—Drop Black—Ivory Black—Mineral Black.
Willow Charcoal.
Black Oxide of Iron.

ANALYSIS OF WHITE PIGMENTS

SUBLIMED WHITE LEAD

Basic Sulphate of Lead. Basic Sulphate—White Lead

This pigment, embracing the daily analysis by the manufacturers of the product of over five months' time, shows the following average composition:

Lead sulphate	76.68%
Lead oxide	17.23
Zinc oxide	5.79
	99.70

The remaining .3 of 1 per cent consists of moisture and ash which are rarely determined.

The analysis of this pigment based on the following method,[1] which depends upon the above average composition, together with the volumetric determination of the total lead and zinc contents, is rapid and accurate.

[1] Jour. of Ind. and Eng. Chem., 6, 3, 200, March, 1914.

Volumetric Determination of Lead [1]

One gram of the sample is dissolved in 100 cc. of an acid ammonium acetate solution made up as follows:

Eighty per cent acetic acid	125 cc.
Concentrated ammonium hydroxide	95 cc.
Water	100 cc.

Add this solution hot, dilute with 50 cc. water and boil until a clear solution is obtained. Dilute to 200 cc. and titrate with standard ammonium molybdate solution, using a freshly prepared solution of tannic acid as an outside indicator.

A solution of ammonium molybdate containing 8.67 grams per liter usually gives a solution where,

One cc. = 0.01 gram Pb.

Standardize against pure PbO, pure $PbSO_4$, or clean lead foil.

For further details of this method see p. 239.

Volumetric Determination of Zinc [2]

Boil 1 gram of the sample with the following solution:

Water	30 cc.
Ammonium chloride	4 grams
Concentrated hydrochloric acid	6 cc.

If the sample is not quite dissolved, the result is unaffected, as the residue is lead sulphate or precipitated lead chloride.

Dilute to 200 cc. with hot water. Add 2 cc. of a saturated sodium hyposulphite solution and titrate with a standard solution of potassium ferrocyanide, using a 5% solution of uranium nitrate as an outside indicator. Calculate the zinc to zinc oxide.

Using the average total of 99.70%, the total lead found and the zinc oxide content, the composition of this pigment is determined by the following calculation:

Total percentage of lead compounds present
= total percentage found of ZnO, PbO and $PbSO_4$ − percentage of ZnO.

Total percentage of lead compounds present
= 99.70% (average total) − percentage ZnO.

Atomic weight lead	207.1
Molecular weight lead oxide	223.1
Molecular weight lead sulphate	303.1

As a hypothetical case, we can assume the presence of a 4.70% ZnO and 69.00% metallic lead.

[1] Modification of Low's Method, "Technical Methods of Ore Analysis," p. 149.
[2] Low's Method, "Technical Methods of Ore Analysis," p. 284.

$$\frac{\left(\frac{\text{Mol. wt. } PbSO_4}{\text{At. wt. Pb}} \times \%\text{ Pb found}\right) - \%\text{ Pb constituents}}{\frac{\text{Mol. wt. } PbSO_4 - \text{mol. wt. PbO}}{\text{Mol. wt. PbO}}} = \%\text{ PbO present}$$

$$\frac{\left(\frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \%\text{ Pb found}\right) - \%\text{ Pb constituents}}{\frac{\text{Mol. wt. PbO} - \text{Mol. wt. } PbSO_4}{\text{Mol. wt. } PbSO_4}} = \%\text{ } PbSO_4 \text{ present.}$$

Determining the percentage of lead oxide and lead sulphate present by the above formulas we find:

$$\frac{\left(\frac{303.1}{207.1} \times 69.00\right) - 95.00}{\frac{303.1 - 223.1}{223.1}} = \text{per cent PbO} = 16.68$$

$$\frac{\left(\frac{223.1}{207.1} \times 69.00\right) - 95.00}{\frac{223.1 - 303.1}{303.1}} = \text{per cent } PbSO_4 = 78.32.$$

If it is necessary actually to determine the percentage of lead sulphate present, the following procedure may be followed:

Total Sulphate

Mix 0.5 gram of the sample with 3 grams of sodium carbonate. Add 30 cc. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute with hot water, filter and wash thoroughly. All the lead sulphate is here changed to lead carbonate, the sodium carbonate being transposed to sodium sulphate, which is found in the filtrate.

The sulphate is determined in the filtrate by precipitation as $BaSO_4$. Calculate the $BaSO_4$ to $PbSO_4$. Determine the total lead as above outlined, deduct the lead found as $PbSO_4$ and calculate the residual lead to PbO.

The foregoing method is the one generally used in the commercial estimation of lead and yields excellent results to the analyst who is familiar with it. However, in laboratories where only occasional lead determinations are made, the well-known gravimetric methods for lead and zinc will sometimes be found preferable. The time required for gravimetric determinations is not much greater and the chance of error is reduced.

The method referred to consists in weighing the lead as sulphate[1] and the precipitation of the zinc from the filtrate with sodium carbonate, igniting it, and weighing as zinc oxide.

[1] As outlined under Basic Carbonate of Lead, p. 625.

CORRODED WHITE LEAD

Basic Carbonate of Lead[1]—Old Dutch Process White Lead—Quick Process White Lead—Mild Process White Lead

Corroded white lead contains approximately 80% metallic lead and 20% carbonic acid and combined water with traces sometimes of silver, antimony and other metals. The formula for this compound is $2PbCO_3 \cdot Pb(OH)_2$.

Total Lead (Gravimetric)

Dissolve 1 gram in 20 cc. of HNO_3 (1:1) in a covered beaker, heating till all CO_2 is expelled; wash off cover, add 20 cc. of H_2SO_4 (1:1) and evaporate to fumes of SO_3, cool, add about 150 cc. of water and 150 cc. of ethyl alcohol; let stand in cold water one hour, filter on a Gooch crucible, wash with 95% ethyl alcohol, dry at 110° C., and weigh the $PbSO_4$. Calculate to PbO or to basic carbonate.[2] Instead of determining the lead as sulphate, the sample may be dissolved by boiling with acetic acid; then dilute to about 200 cc. with water, make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 cc. of a 10% solution of potassium dichromate; heat till the yellow precipitate assumes an orange color. Let settle and filter on a Gooch crucible, washing by decantation with hot water till the washings are colorless, finally transferring all of the precipitate. Then wash with 95% ethyl alcohol and then ether; dry at 110° C. and weigh $PbCrO_4$. (Any insoluble matter should be filtered out before precipitating the lead.)

Total Lead (Volumetric)

Dissolve 0.5 gram of sample in 10 cc. of concentrated hydrochloric acid, boil till solution is effected, cool, dilute to 40 cc. and neutralize with ammonium hydroxide. Add acetic acid until distinctly acid, dilute to 200 cc. with hot water, boil and titrate with ammonium molybdate as follows:

Dissolve 4.25 gram of ammonium molybdate in water and make up to one liter. To standardize this solution, dissolve about 0.2 gram of pure lead foil in nitric acid (pure PbO or $PbSO_4$ may also be used), evaporate nearly to dryness, add 30 cc. of water, then 5 cc. H_2SO_4 (sp.gr. 1.84), cool, and filter.

Drop filter with $PbSO_4$ into a flask, add 10 cc. concentrated HCl, boil till completely disintegrated, add 15 cc. of HCl, 25 cc. of water, and NH_4OH till alkaline. Acidify with acetic acid, dilute to 200 cc. with hot water and boil. Titrate, using an outside indicator of one part of tannic acid in 300 parts of water.

It should be noted that when calcium is present, it forms a more or less insoluble molybdate, and results are apt to be high. With samples containing less than 10% of lead, the lead should be precipitated as $PbSO_4$, filtered, redissolved and titrated as in the process of standardizing.

Carbon Dioxide

Determine by evolution with dilute hydrochloric acid absorbing in soda-lime or KOH solution. Calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

[1] Tentative Methods for the Routine Analysis of White Pigments. Report of Commission D–1, American Society for Testing Materials, 1915.

[2] This method of weighing lead sulphate is not accurate in the presence of calcium compounds.

Acetic Acid [1]

Place 18 grams of the pigment in a 500-cc. flask, add 40 cc. of sirupy phosphoric acid, 18 grams of zinc dust and 50 cc. of water. Connect to a straight Liebig condenser, apply heat and distill down to a small bulk. Then pass steam into the flask until it becomes about half full of condensed water, shut off the steam and distill down to a small bulk—this operation being conducted twice. To the total distillate which was collected in a larger flask add 1 cc. of sirupy phosphoric acid, connect to a Liebig condenser, using a spray trap, and distill to a small volume—about 20 cc. Pass steam through till about 200 cc. of water condense in the distillation flask, shut off steam and continue the distillation. These operations of direct and steam distillations are conducted until 10 cc. of the distillate require only 1 drop of 0.1 N alkali to give a change in the presence of of phenolphthalein. Then titrate the total distillate with 0. 1 N sodium hydroxide and phenolphthalein and calculate the total acidity as acetic acid. It will be found convenient to titrate each 200-cc. portion of the distillate as collected.

Metallic Lead [1]

Weigh 50 grams of the sample into a 400-cc. beaker, add a little water and add slowly 60 cc. of 40% acetic acid and after effervescence has ceased, boil on hot plate. Fill the beaker with water, let settle, and decant the clear solution. To the residue add 100 cc. of a mixture of 360 cc. of strong NH_4OH, 1080 cc. of water, 2160 cc. of 80% acetic acid, and boil until all solution is complete. Fill the beaker with water, let settle and decant the clear solution. Collect residue on a watch-glass, floating off everything but metallic lead. Dry and weigh. Result $\times 2$ = percentage of metallic lead in sample.

The following method of A. N. Finn (unpublished) gives total basicity of a pure white lead: Place 2 grams of pigment in an evolution flask, add a little CO_2-free water, connect with a separatory funnel and condenser (Knorr type), add through the funnel, finally washing down, 100 cc. of N/4 nitric acid, boil and absorb the CO_2 in a soda lime tube in the usual manner (having H_2SO_4 and $CaCl_2$ drying tubes in train) and weigh. To the solution in the evolution flask, add about 20 cc. of neutral sodium sulphate solution and titrate with N/4 sodium hydroxide solution (carbonate-free), using phenolphthalein. CO_2 is calculated to $PbCO_3$. The amount of N/4 acid corresponding to the CO_2 is calculated and deducted from the total amount of N/4 acid neutralized by the sample and the difference calculated to combined H_2O, from which $Pb(OH)_2$ is computed.

ZINC LEAD AND LEADED ZINC

Zinc lead and leaded zinc are varying compounds containing zinc oxide and lead sulphate, the former showing approximately 50% zinc oxide and 50% lead sulphate, while the latter contains on an average 25% lead sulphate and 75% zinc oxide. See also pp. 239, 480.

These pigments may be analyzed by the following procedure:

Moisture. Heat 2 grams at 105° C. for two hours.

[1] Thompson's Method, Jour. Soc. Chem. Ind., **24**, 487 1905.

Lead and Zinc. Determine the lead directly by the volumetric molybdate method and the zinc by the volumetric ferrocyanide method as outlined under Sublimed White Lead. See also pages 239 and 480.

Total Soluble Sulphates[1] (in the absence of $BaSO_4$). Treat 0.5 gram of the sample with 5 cc. of water, 3 grams of NH_4Cl and 5 cc. of HCl saturated with bromine; digest (covered) on the steam bath about fifteen minutes, add 25 cc. of H_2O, neutralize with dry Na_2CO_3 and add about 2 grams more. Boil ten to fifteen minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in HCl, reprecipitate as above and wash thoroughly with hot water. Acidify the united filtrates with HCl and add a slight excess of 10% $BaCl_2$ solution. Let stand on steam bath for one hour, filter, wash with hot water, ignite and weigh the $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2).

Total Soluble Sulphate (in the presence of $BaSO_4$). Treat 1 gram in a 600-cc. beaker with 10 cc. of H_2O, 10 cc. of strong HCl, saturated with bromine, and 5 grams of NH_4Cl, heat on a steam bath in a covered beaker for five minutes, add hot water to make about 400 cc., boil for five minutes and filter to separate any insoluble material. (A pure pigment should be completely dissolved.) Wash with hot water, ignite and weigh the insoluble. Remove lead with Na_2CO_3 as above, making a double precipitation, acidify, and to the boiling hot filtrate add slowly, with stirring, 20 cc. of a 10% $BaCl_2$ solution; let stand for two hours on the steam bath, filter, wash, ignite, and weigh as $BaSO_4$. (Includes SO_3 formed from SO_2.)

Soluble Zinc Sulphate. Boil 2 grams of the sample with 150 cc. of water and 50 cc. of alcohol for thirty minutes, filter and wash with a mixture of alcohol and water (1:3). Heat the filtrate to boiling and expel most of the alcohol; then determine SO_3 by the usual method of precipitation with $BaCl_2$. Calculate to $ZnSO_4$ and to SO_3.

Sulphur Dioxide. Digest 2 grams of the sample with frequent stirring in 100 cc. of freshly boiled cold water and 5 cc. of concentrated HCl; let stand ten to fifteen minutes, add an excess of 0.01 normal iodine solution and titrate back with 0.01 normal sodium thiosulphate solution, using starch indicator. Report as SO_2. Run blank on reagents and make corrections.

Calculations. Report soluble SO_3 as $ZnSO_4$. Deduct ZnO equivalent of the $ZnSO_4$ from total ZnO and report residue as ZnO. Deduct soluble SO_3 and SO_3 equivalent to SO_2 from total SO_3, calculate remainder to $PbSO_4$; subtract PbO equivalent of $PbSO_4$ from total PbO and report remainder as PbO.

ZINC OXIDE[2]

Moisture. Weigh 10 grams on watch-glass and dry for two hours at 105 to 110° C. Cool and weigh.

Carbon Dioxide. Place 10 grams in a 4-ounce Erlenmeyer flask, moisten with water, add solution of $KMnO_4$ to oxidize SO_2, insert a two-hole rubber stopper, with an acid delivery tube and connect to a carbon dioxide apparatus. This apparatus consists of a tube containing KOH solution, preceding the flask with

[1] Report of Sub-committee VIII of Committee D-1, Proceedings of American Society for Testing Materials, 14, 271-2, 1914.

[2] Frank G. Breyer, Chief, Testing Department, The New Jersey Zinc Co.

sample, to absorb any CO_2 from the air drawn in. The flask is followed by a tube with concentrated H_2SO_4 to absorb moisture, a calcium chloride tube, and next is a weighed Geissler [1] bulb with KOH solution, to absorb the CO_2 from the sample; this is followed by another calcium chloride tube which is connected to a suction line. The acid delivery tube contains 25 cc. H_2SO_4 (1 : 1) and before opening the stopcock the suction is applied to insure that the connections are all air-tight; if there is no leak the acid is allowed to flow into the flask and the suction regulated so that the bubbles in the Geissler bulb may easily be counted. The flask is heated cautiously to boiling for a minute or two, the flame removed and the suction allowed to proceed from thirty to forty minutes. The Geissler [1] bulb is then disconnected, placed in the balance for fifteen minutes together with the end calcium chloride tube and then weighed. The KOH solution used for absorption is of the same strength as for carbon in steel.

Insoluble. Treat 10 grams in a 250-cc. beaker with 50 cc. concentrated HCl, evaporate to dryness, take up residue with HCl and water, filter and wash thoroughly with HCl (1 : 4) and hot water. Ignite filter paper and contents in a weighed platinum crucible.

Sulphuric Anhydride; Total S as SO_3. Treat 10 grams with 50 cc. strong HCl and a few cc. of bromine water; boil to expel bromine, filter from insoluble, wash with hot water. Neutralize the excess of HCl with ammonia, keeping the solution slightly acid, heat to boiling and add about 15 cc. of hot $BaCl_2$. Let stand overnight, filter on a weighed Gooch crucible, wash well with hot water, ignite in a muffle, cool and weigh as $BaSO_4$.

Lead Oxide

Gravimetric Method. Treat 10 grams with 50 cc. strong HCl and 50 cc. H_2SO_4 (1 : 1), evaporate on a hot plate, and finally over a Bunsen burner to strong fumes of SO_3.

Cool, and add 100 cc. water, heat again to dissolve the soluble sulphates, cool, add 25 cc. 95% alcohol, let stand overnight, filter on a Gooch crucible and wash with dilute H_2SO_4, and finally with alcohol. Dry at 110° C., ignite for five to ten minutes, cool and weigh. Dissolve the $PbSO_4$ in the Gooch crucible with a hot solution of ammonium acetate, slightly acidify with acetic acid, wash with hot water, dry at 110° C., ignite and weigh again. The loss in weight is $PbSO_4$, from which the PbO is calculated.

Electrolytic Method. 9.330 grams of the sample are dissolved in a 250-cc. beaker with 40 cc. concentrated HNO_3 and about 50 cc. of distilled water. The solution is boiled for a few minutes until all red fumes are expelled. Add enough silver nitrate solution to precipitate all chlorides (an excess of silver nitrate does not interfere) and dilute to about 200 cc.

Electrolyze for two hours, using about .5 ampere current. The solutions are tested for lead before turning off the current by raising the liquid in the beaker, and allowing to continue for twenty minutes. If there is no fresh deposit of PbO_2 the electrode is washed three times with distilled water (current still on) and then after removal from the electrolytic stand, with alcohol. After drying one hour at 110° C. the electrode is weighed. The weight of PbO_2 in milligrams divided by 100 gives the percentage of PbO.

[1] See Procedure for CO_2 determination in the chapter on Carbon, p. 103.

Chlorine. Treat 10 grams of sample with 50 cc. strong HNO_3, add 10 cc. N/10 $AgNO_3$, boil, cool, add 10 cc. ferric nitrate (1 : 3), and titrate the excess of $AgNO_3$ with NH_4CNS (9 grams per liter of solution). A blank determination is conducted in a similar manner and from the amount of N/10 $AgNO_3$ required the chlorine is calculated.

Ferric Oxide. Treat 10 grams with 50 cc. strong HCl, add about 1 gram $KClO_3$, and boil down to a syrupy consistency. Cool, add water and a large excess of ammonia. Allow to stand until the ferric oxide separates, and filter; wash with dilute ammonia water and then with hot water. Dissolve the precipitate of ferric oxide in an Erlenmeyer flask with warm dilute H_2SO_4. Wash the filter paper thoroughly with hot water, dilute the solution in the Erlenmeyer flask to about 200 cc. and pass in hydrogen sulphide for five minutes. Place a funnel in the neck of the flask and boil until all H_2S is expelled. Cool and titrate with dilute $KMnO_4$. A blank determination is carried out in a similar manner and the number of cc. of $KMnO_4$ required to give a pink color is subtracted from the total number required on the sample.

Manganese Oxide. Treat a 10-gram sample in a 16-oz. Erlenmeyer flask with 100 cc. of HNO_3 (1:3), heat to boiling and add a pinch of sodium bismuthate, when the pink color of permanganic acid is produced; now add a few cc. of dilute $Na_2S_2O_3$ solution to destroy the pink color, and continue boiling to drive off all nitrous oxide fumes. Cool thoroughly and add 50 cc. of a 3% solution of HNO_3, and a very small pinch of sodium bismuthate to restore the pink color again. Filter the solution through a Gooch crucible to remove the excess of sodium bismuthate, rinsing the flask and Gooch with 50 cc. of 3% HNO_3 solution to which a small amount of sodium bismuthate has been added. Now add 10 cc. of ammonium ferrous sulphate solution, and titrate the excess of ammonium ferrous sulphate with standard $KMnO_4$ whose iron value has been determined. One gram of $KMnO_4$ per liter is a convenient strength; and 12.4 grams of ammonium ferrous sulphate, and 50 cc. strong H_2SO_4 to the liter gives a solution which is almost equal to the permanganate solution. A blank determination is carried out in exactly the same manner as with the sample of oxide, and the difference in the number of cc. of $KMnO_4$ required to give a pink color with the blank determination and the sample of oxide is equal to the amount of MnO present. The manganese value of the $KMnO_4$ is calculated from the iron value, according to the ratio of Mn : Fe, or 55 : 279.5 or 0.1968 : 1.

Arsenous Oxide. Weigh 10 grams of oxide in a 16-ounce Erlenmeyer flask, add about 10 grams of $FeSO_4$, place a rubber stopper with an acid delivery tube and an exit tube, which is immersed in a beaker containing about 200 cc. distilled water. The beaker of water is placed in a pan of cold water, the pan having an inlet and overflow. Now add 100 cc. strong HCl from the delivery tube, and heat the flask to boiling so as to distill the arsenic into the beaker of water. Continue boiling until about two-thirds of the acid has been distilled, remove from the flame, rinse the delivery tube, add 10 cc. strong HCl to the solution in the beaker, warm and pass in H_2S to precipitate the arsenic, as As_2S_3. Let stand in a warm place for some time and filter in a Gooch crucible, wash the precipitate of As_2S_3 with alcohol and then with carbon bisulphide and several times with dilute alcohol. Dry at 105° C. for one hour and weigh. Dissolve the As_2S_3 in the Gooch crucible with dilute ammonia water, wash well with hot water, and dry at 105° C. and reweigh. The loss in weight is As_2S_3, from which the As_2O_3 may be calculated. See procedure for arsenic distillation, p. 33.

SO_2 Equivalent. Treat 10 grams in a 250-cc. beaker with 25 cc. cold water, 25 cc. hot water, add some starch solution and titrate with N/10 iodine solution, gradually adding 25 cc. HCl until a permanent blue color appears.

Zinc Oxide. The percentage of ZnO is found by adding together all the percentages of impurities, except the SO_2 equivalent, and subtracting this sum from 100.

LITHOPONE

Ponolith—Beckton White—Charlton White, etc.

This pigment is a chemically precipitated pigment containing approximately from 69 to 70 per cent barium sulphate, the remainder consisting of zinc sulphide, with occasional impurities of zinc oxide and carbonate.

Moisture. Heat 2 grams for two hours at 105° C.

Barium Sulphate. Treat 1 gram with 10 cc. conc. HCl and 1 gram of potassium chlorate, added in small amounts. Evaporate to one-half its volume, add 100 cc. hot water and a few cc. of dilute H_2SO_4. Boil, filter, wash and weigh the insoluble residue, which should show only the presence of barium sulphate. Examine the residue for silica and alumina.

Total Zinc. Determine the total zinc in the filtrate by the volumetric method as outlined under Sublimed White Lead.

Zinc Sulphide. Digest 1 gram at room temperature for one-half hour with 100 cc. of 1% acetic acid. Filter and determine the zinc in the precipitate by solution in HCl as under Sublimed White Lead.

Zinc soluble in acetic acid is reported as zinc oxide, zinc insoluble as zinc sulphide. The filtrate from the acetic acid treatment, after precipitating the zinc as zinc sulphide and subsequent removal, should be examined for barium which might be present as carbonate, and calcium, present as either sulphate or carbonate. The zinc sulphide may also be determined by the method as outlined under Tentative Methods for Analysis of Pigments by Committee D-I[1] as follows:

Zinc Sulphide.[2] Place 0.5 gram of the pigment in an evolution flask[3] with about 10 grams of "feathered" or mossy zinc, add 50 cc. of water; insert the stopper carrying a separatory funnel and an exit tube. Run in 50 cc. of concentrated HCl from the funnel, having previously connected the exit tube to two absorption flasks, in series; first flask contains 100 cc. of alkaline lead nitrate solution, second flask, 50 cc. of same as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask. Disconnect, let the lead sulphide settle, filter, wash with cold water, then with hot water till neutral to litmus paper and washings give no test for lead. The PbS precipitate in dissolved in hot, dilute HNO_3, evaporated to fumes with H_2SO_4 and finally weighed as $PbSO_4$. Calculate PbS or $PbSO_4$ to ZnS.

The alkaline lead solution is made as follows: Into 100 cc. of KOH solution (56 grams in 140 cc. of H_2O) pour a saturated solution of lead nitrate (250 grams in 500 cc. of H_2O) until the precipitate ceases to redissolve, stirring constantly

[1] American Society for Testing Materials, 1915.

[2] Evolution Method of W. G. Scott, "White Paints and Painting Material," p. 257; see also p. 398, chapter on Sulphur by W. W. Scott.

[3] See Apparatus on p. 399.

while mixing. About three volumes of the lead solution will be required for one of the alkali.

Instead of absorbing the evolved H_2S in alkaline lead-nitrate solution, a solution of 8 grams of cadmium chloride in 250 cc. of water and 150 cc. of NH_4OH (sp.gr. 0.90) may be used. The CdS precipitate may be filtered on a weighed Gooch, washed with water containing a little NH_4OH, dried at 100° C., and weighed. Calculate to ZnS. It is better to filter the CdS on a small filter and wash as above, then place filter and precipitate in a beaker and dissolve in HCl and $KClO_3$ (keeping at room temperature at first). Filter out any paper pulp or insoluble matter, make filtrate alkaline with NH_4OH, then just acid with HCl, heat to boiling and precipitate with $BaCl_2$ in the usual manner. Filter, wash, ignite, and weigh the $BaSO_4$. Calculate to ZnS.

For very rapid work the contents of the absorption flask, after all H_2S has been absorbed, may be washed into a vessel with cold water and diluted to about 1 liter, acidified with concentrated HCl and titrated with standard iodine solution, using starch indicator. (The precipitate should be completely dissolved.) The iodine solution is prepared by dissolving about 12.7 grams of pure resublimed iodine and 18 grams of KI in a little water and then diluting to 1 liter.

Soluble Salts. Digest 2 grams with hot water and examine the filtrate for soluble salts.

SILICA OR SILEX—CHINA CLAY—ASBESTINE

These pigments, while all true silica pigments, are widely different from the standpoint of physical structure. A microscopic examination is of great value, showing silica or silex to consist of small, sharp particles, china clay to be tabloid in appearance and asbestine to consist of long, rod-like fibrous particles.

The following procedure taken from the outlined method published by Sub-Committee VIII of Committee D-I [1] will well serve for the analysis of these pigments.

Moisture. Heat 2 grams at 105° for two hours.

Loss on Ignition. Ignite 1 gram to constant weight in a platinum crucible.

Insoluble Matter. Boil 2 grams for thirty minutes with 50 cc. HCl (1 : 1), add 50 cc. of water, wash, ignite, and weigh insoluble residue.

In the case of China clay, or asbestine, a sodium carbonate fusion should be resorted to, with the subsequent dehydration of the silica.

The insoluble residue in either case is volatilized with H_2SO_4 and HF in the usual manner, any loss in weight being considered silica. Any residue is fused with sodium carbonate, the fusion being added to the original filtrate. Should $BaSO_4$ be present, the melt is digested with warm water, the $BaCO_3$ filtered off, washed, dissolved in hot dilute HCl and precipitated and determined as $BaSO_4$.

The filtrates, combined from the preceding filtrations, are examined for alumina, iron, manganese, calcium and magnesium in the usual way.

Should it be necessary to determine the alkalies present, a separate sample is treated according to the method of Mr. J. Lawrence Smith as in Bulletin No. 422, U. S. Geological Survey.

Carbon Dioxide. Determine by evolution with HCl, weighing in soda-lime, KOH solution, or by absorbing in $Ba(OH)_2$ solution and titrating or weighing as $BaCO_3$. See p. 103.

[1] Proceedings of American Society for Testing Materials, 14, 279, 1914.

Any excess of calcium is reported as oxide. The magnesium is calculated as MgO, unless the carbon dioxide is in excess of the amount of calcium present, in which case it is reported as $MgCO_3$, and the remainder as MgO.

WHITING—PARIS WHITE

Gypsum—Plaster of Paris

These pigments are of the following composition:

Whiting. The natural form of calcium carbonate.

Paris White. The artificial form of calcium carbonate.

Gypsum. The hydrated form of calcium sulphate, of formula $CaSO_4 \cdot 2H_2O$.

These pigments are analyzed in the following manner:

Moisture. Heat 2 grams at 105° C. for two hours.

Loss on Ignition. Ignite 1 gram at a high heat to constant weight. The loss will be water, if carbonates are absent.

Calcium. Treat 1 gram with dilute HCl and a few drops of HNO_3. Evaporate to dryness, dehydrate, moisten with a few drops of concentrated HCl, dilute with hot water and determine the insoluble residue. Examine for $BaSO_4$. The residue should consist of silica.

In the filtrate, precipitate and determine the iron hydroxide and aluminum hydroxide in the usual manner. The calcium is precipitated in the boiling ammoniacal filtrate with 30 cc. of saturated ammonium oxalate solution, allowing the solution to boil for one-half hour. A double precipitation is here advisable to remove the last traces of magnesium. The calcium oxalate is filtered off, thoroughly washed and determined volumetrically by the permanganate method, p. 92.

Magnesium. Determine in the filtrates after removal of the calcium by precipitation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate in the usual manner, p. 255.

Carbon Dioxide. Determine as outlined under Silica.

Sulphates. Dissolve 1 gram in concentrated HCl, remove any insoluble residue, heat to boiling and precipitate any sulphate as $BaSO_4$, determining in the usual manner. See p. 395.

BARYTES AND BLANC FIXE

Of these two barium pigments used in the manufacture of paints, barytes is the natural barium sulphate, while blanc fixe is precipitated barium sulphate. Their barium sulphate content should be not less than 95%.

The following method may be used for the analysis of these pigments:

Moisture. Heat 2 grams at 105° C. for two hours.

Loss on Ignition. Ignite 1 gram to constant weight. The loss will be reported as loss on ignition, and will consist of free and uncombined water, carbon dioxide and organic matter.

Barium Sulphate. Boil 1 gram with dilute HCl, evaporate to dryness, moisten with HCl, add water, boil, filter and wash. Should lead be present in the insoluble residue, as shown by the action of H_2S, treat the insoluble residue with a little (1 : 1) HCl and several drops of H_2SO_4. Filter, wash and weigh the residue. Treat the ignited residue with H_2SO_4 and HF, evaporate to dryness

and ignite. The residue should show no loss as silica. The filtrate is examined for alumina, iron, calcium and magnesium in the usual manner.

Soluble Sulphates. Treat 1 gram with 20 cc. conc. HCl, dilute to 200 cc. with hot water, boil, filter, wash, add NH_4OH until neutral, make acid with HCl and precipitate any sulphate as $BaSO_4$. Determine in the usual manner. Calculate to $CaSO_4$. If carbonates are present, calculate the remaining CaO to $CaCO_3$. Any excess of oxide is reported as CaO.

Carbon Dioxide. Determine as outlined under silica. If any barium carbonate is present, it is determined in the filtrate from the preliminary HCl treatment, by precipitation and weighing, as $BaSO_4$. Any excess of carbon dioxide over the barium is reported as calcium carbonate.

ANALYSIS OF A COMPOSITE WHITE PAINT

A white paint may consist of a mixture of any of the preceding pigments, excepting that it is understood that lead pigments and lithopone are seldom found together, owing to their tendency to blacken with the formation of lead sulphide.

After separation from the oil and other liquids as outlined above, the white pigment mixture may be rapidly analyzed by the following method. It is, however, often advisable to resort to a qualitative examination before beginning the quantitative analysis.

Insoluble Residue. Boil 1 gram of the sample with 20 cc. (1 : 1) HCl. Evaporate to dryness, moisten the residue with a few cc. of concentrated HCl, allow to stand a few minutes, dilute with hot water, boil, filter and wash the insoluble residue thoroughly with hot water. Treat the insoluble residue with (1 : 1) HCl and 2 cc. H_2SO_4 to remove the last traces of lead. Filter, wash and weigh the insoluble residue. Determine the silica by volatilization with H_2SO_4 and HF. Any loss is reported as silica. Determine the $BaSO_4$ in the residue by boiling with dilute HCl or making a potassium bisulphate fusion. The residue remaining after either of these treatments is reported as barium sulphate.

Total Lead. This constituent can be best determined on a separate sample. To 1 gram add 10 cc. of conc. HNO_3, boil, add, after cooling, conc. H_2SO_4 and evaporate to strong SO_3 fumes. Dilute with water, allow to stand several hours, filter, wash slightly, dissolve and determine the lead volumetrically as outlined under Sublimed White Lead.

Lead can also be determined on the combined filtrates from the insoluble residue. Precipitate the lead in an acid solution with H_2S and determine volumetrically in the above outlined manner.

To determine whether both sublimed white lead and corroded white lead are present, treat a separate portion of the paint with boiling acetic acid, filter and collect the insoluble residue. Determine the lead either in the filtrate or in the insoluble residue by the volumetric method. The lead soluble in acetic acid is the basic carbonate of lead and the lead oxide from the sublimed white lead, while the lead sulphate from the sublimed white lead remains insoluble.

Alumina and Iron Oxide. Remove the H_2S from the filtrate by boiling, after removal of the lead, and precipitate the hydroxides in an ammoniacal solution after boiling with the addition of a few drops of HNO_3. Determine and separate in the usual manner.

Zinc. Precipitate the zinc in the filtrate from the alumina and iron precipitation, after acidifying with acetic acid, and determine the zinc as outlined under Sublimed White Lead on p. 623.

Calcium and Magnesium. Determine the calcium and magnesium in the filtrate from the precipitation of zinc sulphide in the usual manner, testing, however, first for the presence of barium.

Sulphate. Determine as outlined under Zinc Lead and Leaded Zincs.

Sulphide. Should lithopone be present, separate the zinc oxide and zinc sulphide as outlined under Lithopone, p. 630.

Carbon Dioxide. Determine as outlined under Silica, p. 631.

Calculations. Silica is reported as silica, except where alumina is present, showing the presence of China clay. In this case, calculate the alumina to clay by the method of Scott.

Weight of $Al_2O_3 \times 2.5372$ = weight of clay.

Weight of clay $\times 0.4667$ = weight of SiO_2 in clay.

Any difference greater than 5% may be considered silica.

Barium sulphate is reported as barium sulphate or as lithopone, if zinc sulphide is present, according to the given composition of lithopone, 70% barium sulphate and 30% zinc sulphide.

Lead is reported as Basic Carbonate of Lead on the formula $2PbCO_3 \cdot Pb(OH)_2$.

Calculate lead soluble in acetic acid, after determining CO_2 to basic lead carbonate and any residual lead to lead oxide which, together with the lead sulphate is reported as Sublimed White Lead.

Should calcium sulphate be present the portion soluble in water is examined for lime or sulphuric acid and calculated to calcium sulphate, any residual lime being calculated to calcium carbonate and any residual sulphuric acid being calculated to lead sulphate. Any residual CO_2 after calculating calcium carbonate is calculated to white lead and any residual lead is calculated to lead oxide.

Lead oxide should not be reported except in the presence of lead sulphate. Any large percentage of magnesium denotes the presence of asbestine.

RED AND BROWN PIGMENTS

These pigments are grouped under these heads:

The Lead Oxide Pigments—The Iron Oxide and Manganese Oxide Pigments—The Mercury Oxide Pigments

RED LEAD AND ORANGE MINERAL

These pigments in the pure form are oxides of lead, of the generally accepted form, Pb_3O_4, being probably mixtures of lead monoxide, and lead dioxide. In chemical composition they are the same, the proportions of lead monoxide and lead dioxide varying, however, but by their physical structure and color they can be readily differentiated.

Two methods are given for the analysis of this pigment. The first is taken from the method as outlined by Sub-committee VIII of Committee D-I.[1]

Moisture. Dry 2 grams at 105° for two hours.

[1] Proceedings of American Society for Testing Materials, 14, 281–283, 1914.

Organic Color. Boil 2 grams with 25 cc. of 95% ethyl alcohol, let settle, decant off the supernatant liquid; boil residue with water, decant as before and boil residue with very dilute NH_4OH. If either the alcohol, water or NH_4OH is colored, organic coloring matter is indicated.

Total Lead and Insoluble Residue. Treat 1 gram with 15 cc. of HNO_3 (1 : 1) and sufficient hydrogen dioxide to dissolve all the PbO_2 on warming. If any insoluble matter is present, add 25 cc. of water, boil, filter and wash with hot water. Insoluble contains free SiO_2, and should be examined for $BaSO_4$ and silicates, if appreciable. To the original solution or filtrate from insoluble, add 20 cc. of conc. H_2SO_4 and evaporate to SO_3 fumes; cool and determine lead as lead sulphate either gravimetrically or volumetrically. If the sample contains soluble barium salts, the $PbSO_4$ will contain $BaSO_4$ and should be treated with acid-ammonium acetate solution, the lead being determined in the filtrate.

Determination of Lead Peroxide (PbO_2) and True Red Lead (Pb_3O_4). (Method of Diehl,[1] modified by Topf[2]—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)

Weigh 1 gram of finely ground sample into a 200-cc. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 grams of C.P. "Tested Purity" crystallized sodium acetate, 2.4 grams of C.P. potassium iodide, 10 cc. of water and 10 cc. of 50% acetic acid; stir until all is liquid, warming gently; if necessary add 2 to 3 cc. of H_2O, cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 cc. of water containing 5 or 6 grams of sodium acetate, and titrate at once with decinormal sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off rod, add the sodium thiosulphate solution until pale yellow, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of thiosulphate that had been added.

Calculation. The iodine value of the sodium thiosulphate solution multiplied by $0.94193 = PbO_2$; the iodine value multiplied by $2.69973 = Pb_3O_4$; the PbO_2 value multiplied by $2.86616 = Pb_3O_4$.

Sodium Thiosulphate Solution (decinormal). Dissolve 24.83 grams of C.P. sodium thiosulphate, freshly pulverized and dried between filter paper, and dilute with water to 1 liter at a temperature at which the titrations are to be made. The solution should be made with well-boiled H_2O, free from CO_2, or let stand eight to fourteen days before standardizing. Standardize with pure, resublimed iodine, as described in the chapter on Iodine, page 204, and also against pure potassium iodate. The two methods of standardization should agree within 0.1% on iodine value.

Starch Solution. Two to 3 grams of potato starch are stirred up with 100 cc. of 1% salicylic acid solution, and the mixture boiled till the starch is practically dissolved and then diluted to 1 liter.

The red lead may also be examined for zinc, carbon dioxide, and soluble sulphate.

[1] Dingl. Polyt. Jour., **246**, 196.
[2] Zeitschrift für analytische Chemie, **26**, 296.

The second method for determination of the lead peroxide or true red lead content is somewhat shorter.[1]

Treat 1 gram in a beaker with 15 cc. of nitric acid, sp.gr. 1.2 (110 cc. nitric acid, sp.gr. 1.42 to 100 cc. of water). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 cc. of dilute hydrogen dioxide (1 part of 3% hydrogen dioxide to 3.5 parts of water). Add about 50 cc. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 cc. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen dioxide solution must now be made.

Into a beaker pour 15 cc. of nitric acid of above strength and add exactly the same amount of hydrogen dioxide (10 cc.). Dilute to 250 cc. with hot water and titrate with standard potassium permanganate solution to a faint pink color.

The difference between the number of cc. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount required for the hydrogen dioxide which was reacted on by the red lead. The difference between the two amounts of potassium permanganate required multiplied by 3.058 grams gives the percentage of red lead present. The difference multiplied by 1.067 gives the percentage of PbO_2 present.

VERMILION

The following portion of Walker's[2] method, will suffice for the examination of this pigment. Should the analyst desire to determine the sulphide of mercury present or make a more complete examination—reference may be made to the original method.

True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1%. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a mufflle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury.

Genuine vermilion is at the present time little used in paints. Organic lakes are used for most of the brilliant red, scarlet and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral or zinc oxide; but as a usual thing the base is barytes, whiting or china clay. Paranitraniline red, a compound of diazotized paranitraniline and beta-naphthol, is largely employed; but a number of colors may be used.

Paranitraniline red is soluble in chloroform. It is also well to try the solvent

[1] "Analysis of Lead and Its Compounds," Schaeffer and White, pp. 25–27.

[2] P. H. Walker, Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. of Agr., pp. 31–33.

action on different reds, of sodium carbonate, etc. The amount of organic pigment present in such reds is generally very small, and when it cannot be determined by ignition owing to the presence of lead, zinc or carbonate, it is best determined by difference.

IRON OXIDES

The iron oxides and manganese oxide pigments include the ochres, umbers, siennas, Venetian red, metallic brown, Indian red and Tuscan red.

In analyzing these pigments, the following constituents are sought; moisture, loss on ignition, insoluble residue, iron oxide, manganese dioxide, calcium and magnesium oxides and sulphur trioxide.

Owing to the similarity of the methods used for the analysis of these pigments to those used in the analysis of iron ores, the analyst is referred to p. 211 on the Analysis of Iron Ores, or to the method of Walker.[1]

BLUE PIGMENTS

In examining blue pigments, only three are found of commercial importance in the manufacture of paints; namely, Prussian blue, ultramarine blue and sublimed blue lead.

Sublimed blue lead is the fume product resulting from the smelting of lead ores. In composition it consists of lead sulphate, lead sulphide, lead sulphite, lead oxide and zinc oxide, with occasional traces of carbon. It is finding its greatest use as an inhibitive pigment for the protection of iron and steel. Its color is a bluish gray.

Prussian blue is the double iron and potassium salt of hydroferrocyanic and hydroferricyanic acids.

Ultramarine blue is essentially a silicate and sulphide of sodium and aluminum.

ULTRAMARINE BLUE

Moisture. Heat 2 grams at 105° C. for two hours.

Silica. Digest 1 gram with 30 cc. of concentrated HCl, taking care to avoid spattering. Evaporate to dryness, dehydrate, moisten with conc. HCl, dehydrate a second time, dilute, filter, and determine the silica by volatilization with H_2SO_4 and HF.

Aluminum Oxide. In the filtrate from the silica, precipitate the aluminum hydroxide and determine in the usual manner. Report as aluminum oxide.

Sodium Oxide. The filtrate, after the removal of the aluminum hydroxide is acidified with H_2SO_4. Evaporate to dryness, ignite at a low red heat, and weigh the sodium sulphate. Calculate to sodium oxide.

Total Sulphur. Fuse 1 gram with a mixture of KNO_3 and Na_2CO_3. Dissolve the fused mass in HCl, boil with conc. HNO_3 for one-half hour, remove the insoluble residue and determine the sulphuric acid in the usual way. See p. 628.

Sulphur Present as Sulphate. Dissolve 1 gram in dilute HCl and boil until all the hydrogen sulphide is removed. Filter off the insoluble residue and determine the sulphate in the filtrate.

[1] Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. Agri., pp. 33–34.

PRUSSIAN BLUE—(CHINESE BLUE)—ANTWERP BLUE

Moisture. Heat 2 grams at 105° C. for two hours. Dry Prussian blue should contain less than 7% moisture.

Nitrogen. Determine the nitrogen present by the Kjeldahl-Gunning method.

Iron and Aluminum Oxides. Ignite 1 gram at a low temperature, sufficient to decompose all the blue, but not to render the iron difficultly soluble. Digest the residue with (1 : 1) HCl. Any insoluble residue is examined for silica, barium sulphate and alumina. A pure Prussian blue should show no insoluble residue. The filtrate is examined for alumina, iron and calcium in the usual way.

An aliquot portion of the filtrate after the removal of the calcium is examined for the alkaline metals. Calculate any alkaline metal present to sulphate.

Sulphuric Acid. Determine the sulphuric acid in an aliquot portion after removal of the calcium.

Commercial Analysis. The method of Parry and Coste[1] is sufficiently accurate to determine the Prussian blue in most instances.

By multiplying the percentage of iron by 3.03 or the percentage of nitrogen by 4.4, the percentage of Prussian blue is directly determined.

In the case of Chinese blue, tin salts are frequently found. The presence of these salts should be sought by a qualitative examination.

SUBLIMED BLUE LEAD[2]

Total Lead. The total lead content is determined by the volumetric method for lead as outlined under Sublimed White Lead.

Total Sulphur. Treat 0.5 gram with 10 cc. of water and a few cc. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil, and continue the treatment until the sediment has become white in color. Add 8 cc. of nitric acid, evaporate until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. Determine as outlined under Zinc Lead and Leaded Zinc.

Lead Sulphate. On a separate sample determine the sulphate directly as outlined under Zinc Lead and Leaded Zinc, without any preliminary treatment for the oxidation of sulphites and sulphides.

Lead Sulphite. Boil $1\frac{1}{2}$ grams with 3 grams of sodium carbonate. Allow to stand, filter and thoroughly wash. Treat the filtrate with bromine water as outlined under Total Sulphur and determine the combined sulphur present as sulphate and sulphite. Deduct the amount present as sulphate and calculate to sulphite.

Lead Sulphide. Deduct the sulphur present as sulphate and sulphite from the total sulphur and report the difference as lead sulphide.

Lead Carbonate. Determine any CO_2 present by the evolution method and calculate to lead carbonate. See p. 103.

Lead Oxide. Deduct the lead present as sulphate, sulphite, sulphide and carbonate from the total lead and report the difference as lead oxide.

[1] The Analyst, **21**, 225–230, 1896.

[2] "The Chemical Analysis of Lead and its Compounds," Schaeffer and White, pp. 22–24.

Zinc Oxide. Determine the zinc volumetrically as outlined under Sublimed White Lead and report as zinc oxide.

Carbon and Volatile Matter. Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference in weight as carbon and volatile matter.

YELLOW AND ORANGE PIGMENTS

Chrome Yellows—American Vermilion—Basic Lead Chromate

The pigments under this class all contain chromates, with the exception of orange mineral, which is analyzed as under Red Lead. Frequently they contain lead sulphate and sometimes lead carbonate. A pure chrome yellow should contain only lead chromate and insoluble lead compounds. Owing to the frequent use of organic colors to brighten up the pigment, it is essential that a test be made for organic colors as outlined under Vermilion.

The analysis of these pigments is carried out in the following manner:

Moisture. Heat 2 grams at 105° C. for two hours.

Insoluble Residue. Treat 1 gram with 25 cc. of concentrated HCl, boil and during the boiling add a few drops of alcohol, one at a time. The solution is diluted to 100 cc., the boiling is continued for ten minutes and any insoluble residue is filtered off, thoroughly washed and examined for silica, barium sulphate and alumina.

Lead. The solution is nearly neutralized with NH_4OH and the lead is precipitated as PbS with H_2S. Filter off the precipitate of PbS, dissolve in HNO_3, add H_2SO_4, boil to strong fumes and determine as outlined under Sublimed White Lead or weigh as $PbSO_4$.

Chromium. The filtrate from the lead precipitation is boiled until all the H_2S is driven off. The solution is rendered alkaline with NH_4OH and the chromium is precipitated and determined as chromic oxide. Calculate to chromic anhydride.

Zinc, Calcium and Magnesium. Precipitate the zinc in the filtrate with H_2S and determine as previously outlined, either volumetrically or gravimetrically.

In the filtrate from the zinc precipitation, determine the calcium and magnesium in the usual manner.

If any carbonates are present, determine by the evolution method.

Sulphuric Acid. Determine the total sulphate as outlined under Zinc Lead and Leaded Zinc on p. 627.

Calculations. Any chromic anhydride is calculated to lead chromate, sulphuric acid to lead sulphate, if calcium sulphate is absent, and any residual lead is calculated to lead oxide.

GREEN PIGMENTS

Chrome Green

Green pigments are usually mixtures of chrome yellow and Prussian blue, though organic color is sometimes present, which may be determined by an extraction with alcohol.

A microscopic examination should be made to determine whether the green is a combined precipitation product, which is of the greater value, or one mixed

after separate precipitation. A good green will show the presence of green and blue particles, while a poor green will show yellow and blue particles mixed with green. The analysis may be carried out as follows:[1]

Moisture. Heat 2 grams at 105° C. for two hours.

Insoluble Residue. Heat 1 gram at a low heat until the blue color has been decomposed, keeping the temperature sufficiently low so as not to render any of the iron or lead chromate insoluble. Determine the insoluble residue as outlined under Yellow Pigments, on p. 639.

Lead. Determine as outlined under Yellow Pigments.

Iron, Alumina and Chromium. All the H_2S is expelled from the filtrate after the lead precipitation by boiling. Add a few drops of HNO_3, boil a few minutes and precipitate the aluminum, iron and chromium hydroxides with NH_4OH. Filter, wash, dissolve the precipitate in HCl, and make up the solution to a definite volume.

In one portion the three hydroxides are precipitated together with NH_4OH and weighed. Another portion is treated in a flask with an excess of KOH and bromine water until the iron hydroxide has assumed its characteristic reddish-brown color. Dilute with water, filter, wash and determine the iron in the usual way. Render the filtrate from the iron precipitation acid with HNO_3, precipitate the aluminum hydroxide with NH_4OH and weigh as Al_2O_3.

Chromium is determined in the filtrate by reduction to a chromic salt with HCl and alcohol, precipitated with NH_4OH and weighed as oxide. Any method for the separation of the above hydroxides may be used in place of the one outlined.

Calcium and Magnesium. These constituents are determined in the filtrate from the precipitation of the above hydroxides.

Sulphuric Acid. One gram after ignition until all the blue has been decomposed, is dissolved in 30 cc. of conc. HCl, diluted with water, boiled, filtered, and washed. The sulphuric acid is determined in the filtrate.

Nitrogen. Determine as outlined under Prussian Blue.

Calculation. The Prussian blue is determined by multiplying the iron found by 3.03 or the nitrogen formed by 4.4. The sulphate is calculated to lead sulphate and calcium sulphate, should calcium be present, and the chromium to lead chromate.

BLACK PIGMENTS

The black pigments include those which contain carbon as their essential constituent. The introduction of many black pigments which are made from asphaltic and coal-tar mixtures complicates their chemical analysis. For those pigments which contain coal-tar mixtures, recourse may be had to works[2] covering this matter thoroughly.

The analysis of the simple black pigments may be carried out in the following way:

Moisture. Dry 2 grams at 105° C. for two hours.

Oil. Extract 2 grams, with ether in a fat-extraction apparatus.

Carbon. Determine the carbon by difference after determining the moist-

[1] "The Analysis of Paints," Gardner, Schaeffer, [illegible] of Paints,"

[2] Allen's "Commercial Organic [illegible]" Gardner and Schaeffer.

ure, oil and ash. For an exact determination of carbon make a combustion test, absorbing the carbon dioxide in soda-lime or caustic potash as usual.

Ash. Ignite 2 grams to a bright red heat until all the carbon is driven off. If graphite is present, the ignition must be carried out with the aid of oxygen. Should carbonate be present, mix the ash with a small amount of ammonium carbonate and again ignite, thus reconverting to carbonate any oxide which may have been decomposed.

Analysis of Ash. The ash is boiled with concentrated HCl and the insoluble residue determined in the usual manner. The filtrate is examined for calcium, magnesium and phosphoric acid.

Calculate the magnesium to phosphate, any residual phosphoric acid to calcium phosphate and any residual calcium to carbonate.

COMPLEX COMPOUNDS—FERRO AND FERRI CYANIDES

Hydroferrocyanic Acid

One gram of the hydroferrocyanide in 100 cc. of water acidified with 10 cc. of sulphuric acid is titrated in a casserole with standard potassium permanganate to a permanent pink color. The end-point is poor, so that it is advisable to standardize the permanganate against pure potassium ferrocyanide.

Reaction: $2H_4Fe(CN)_6+O=H_2O+2H_3Fe(CN)_6$

One cc. N $KMnO_4=0.3683$ gram $K_4Fe(CN)_6$.

Hydroferricyanic Acid

Ten grams of hydroferricyanide are dissolved in water, the solution made alkaline with KOH and heated to boiling and an excess of ferrous sulphate solution added. The yellowish brown ferric hydroxide turns black with excess of ferrous salt. The solution is diluted to exactly 500 cc. and 50 cc. of a filtered portion titrated with potassium permanganate.

One cc. N $KMnO_4=.3292$ gram $K_3Fe(CN)_6$.

CEMENT

RICHARD K. MEADE[1]

ANALYSIS AND TESTING OF CEMENTS

The tests ordinarily applied to Portland cement are as follows:

Fineness.
Specific gravity.
Setting time.
Soundness.
Tensile strength.

Chemical analysis is also made, particular attention being paid to the determination of magnesia, sulphur trioxide, and loss on ignition. As a general rule, however, it may be said that so far as the consumer is concerned, more attention is paid to the physical tests than to chemical analysis.

Standard specifications covering the requirements for cement, both chemical and physical, have been adopted by the American Society for Testing Materials, and by the U. S. Government. The former are generally recognized by cement users as the standard requirements, while the latter are used by the various branches of the federal government.

The methods of making these tests follow.

PHYSICAL TESTING

Fineness. The fineness of cement is usually determined by sieving a weighed portion through sieves having openings of definite sizes and observing the percentage of residue caught upon these. The standard sieves for cement testing are the No. 100 and the No. 200. The No. 100 cement test sieve has 100 openings to the linear inch and is called the 100-mesh sieve. Since the size of these openings will be influenced by the size of the wire used to weave the cloth of the sieve, the No. 100 sieve is made of wire having a diameter of 0.0045 in. As it is practically an impossibility to obtain wire having exactly 100 meshes to the linear inch, any sieve will be considered standard which contains from 96 to 100 meshes to the linear inch and is made of brass wire of the proper diameter (0.0045 inch). Similarly the No. 200 sieve (200-mesh) should contain between 188 and 200 meshes to the linear inch and be made of brass wire 0.0024 in. in diameter. The spacing should be regular, and in purchasing a new lot of sieves the number of meshes in each should be counted, and the cloth examined for irregularities. The sieves should be about 8 ins. in diameter, 2½ ins. deep and provided with a cover and a pan 2 ins. deep. The standard specifications and the U. S. Government specifications require the following degrees of fineness:

[1] Chemical, Mechanical and Industrial Engineer, Baltimore, Md.

Portland Cement.

Residue on No. 100 sieve, not over	8%
Residue on No. 200 sieve, not over	25%

Natural Cement.

Residue on No. 100 sieve, not over	10%
Residue on No. 200 sieve, not over	30%

The method of making the test is as follows: The cement to be tested is dried for one hour, in an air bath, at a temperature of from 100 to 110° C. (212 to 230° F.); 50 grams of this are then weighed into the No. 200 sieve, which should also contain a few large (B.B. size) buck-shot and have its pan attached. The cover is now placed on the sieve and the latter held in one hand, in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 200 strokes per minute. The operation is continued until not more than one-tenth of 1% (0.05 gram) passes through after one minute of continuous sieving. The residue is then weighed, placed on the No. 100 sieve and the operation repeated. The results should be reported to the nearest tenth of 1%.

Specific Gravity. The standard instrument for determining specific gravity is the one designed by Le Chatelier, which is shown in Fig. 93. This consists of a flask of 120 cc. capacity, the neck of which is about 20 cm. long. In the middle of this neck is a bulb, above and below which are two marks. The volume between these marks is 20 cc., and the neck, which has a diameter of 9 cm., is graduated into tenths of cc. above the bulb.

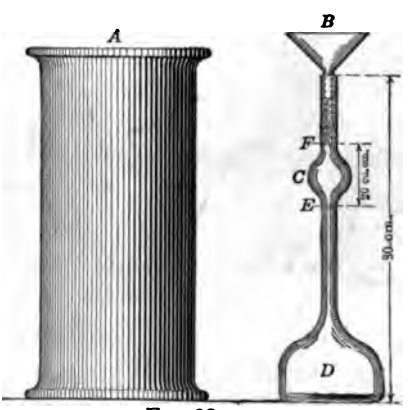


FIG. 93.
Le Chatelier's Specific Gravity Apparatus.

In making the determination, which can be done in either of two ways, benzine (62° Bé. naphtha) or kerosene free from water should be used, and the sample of cement should be dried for at least one hour at from 100 to 110° C. and cooled to room temperature. To make the test fill the flask to the mark *E* with the liquid, next weigh out exactly 64 grams of cement and introduce into the neck of the flask by means of a funnel. The funnel stem should reach below the mark, *F*, on the stem, so that should any of the liquid fall against the side of the neck, it will be below the space eventually occupied by the liquid. The cement is added cautiously towards the last until the liquid fills the bulb, *C*, and rises to the mark, *F*, on the stem. The remainder of the cement is then weighed, and from this the weight of cement which displaces 20 cc. is calculated. From which

$$\text{Specific gravity} = \frac{\text{Difference}}{20}.$$

Instead of the above method the operator may add the entire 64 grams of cement. This will bring the surface of the liquid to one of the divisions on the

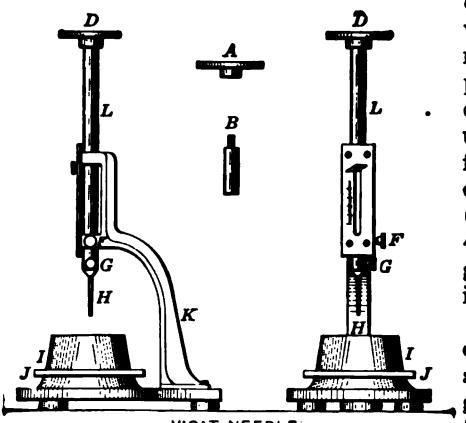
neck above the mark, *F*. This reading on the neck plus 20 will give the number of cc. displaced by 64 grams of cement. Then:

$$\text{Specific gravity} = \frac{64}{20 + \text{Reading on neck}}.$$

Care must be taken to keep the temperature of the liquid constant during the test.

Both sets of specifications require a specific gravity of at least 3.10.

Normal Consistency. In order to properly make the pastes and mortars used in the following tests, the amount of water to be used to make a paste or mortar of a definite state of plasticity, called "Normal Consistency," must be determined. The "standard specification" prescribes for doing this the Vicat needle. This consists of a frame, *K*, Fig. 94, bearing a movable rod, *L*, with the cup, *A*, at one end, and at the other, the cylinder, *B*, 1 cm. (0.39 in.) in diameter, the cap, rod, and cylinder weighing 300 grams (10.58 oz.). The rod, which can be held in any desired position by a screw, *F*, carries an indicator, which moves over a scale (graduated to centimeters) attached to the frame, *K*. The paste is held by a conical, hard rubber ring, *I*, 7 cm. (2.76 ins.) in diameter at the base, 4 cm. (1.57 ins.) high, resting on a glass plate, *J*, about 10 cm. (3.894 ins.) square.



VICAT NEEDLE.
FIG. 94.

The cement is weighed and placed on the mixing slab, which should be about 24 ins. square, and of plate glass or sheet brass. A crater is then formed in the center, into which the proper percentage of clean water is poured, and the material turned into this crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by a vigorous kneading with the hands, for one and a half minutes, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. The hands should be protected by rubber gloves.

The paste is now formed into a ball, pressed into the rubber ring, through the larger opening, smoothed off and placed (on its large end) on a glass plate and the smaller end smoothed off with a trowel. The paste, confined in the ring, and resting on the glass plate, is placed under the rod having the cylinder, which is brought in contact with the surface and quickly released. The paste is of normal consistency when the cylinder penetrates to a point in the mass 10 mm. below the top of the ring. Great care should be taken to fill the ring exactly to the top.

Probably the majority of cement testers determine normal consistency by the ball test. This consists in forming the paste into a ball and dropping it

onto the table from a height of 18 ins. If of normal consistency the ball will neither flatten nor crack—the former if too wet and the latter if too dry. Most cements require about 20 to 24% of water for normal consistency.

The proper percentage of water for sand mortar is found from the following table, the first column of which gives the percentage of water found by trial as above to give normal consistency, and the second column shows the percentage of water for sand mortar.

PERCENTAGE OF WATER FOR STANDARD SAND MORTAR

Neat.	One cement, three standard Ottawa sand.	Neat.	One cement, three standard Ottawa sand.	Neat.	One cement, three standard Ottawa sand.
15	8.0	23	9.3	31	10.7
16	8.2	24	9.5	32	10.8
17	8.3	25	9.7	33	11.0
18	8.5	26	9.8	34	11.2
19	8.7	27	10.0	35	11.3
20	8.8	28	10.2	36	11.5
21	9.0	29	10.3	37	11.7
22	9.2	30	10.5	38	11.8

Setting Time. In making the test, a paste of normal consistency is moulded and placed under the rod, *L*, Fig. 94, as described above; this rod, bearing the cap, *D*, at one end and needle, *H*, 1 mm. (0.039 in.) in diameter, at the other, weighing 300 grams (10.58 oz.) The needle is then carefully brought in contact with the surface of the paste and quickly released.

The cement has its *initial set* when the needle ceases to pass a point 5 mm. above the glass plate, and its final set the moment the needle ceases to sink visibly into the mass.

A simpler test, devised by Gen. Gilmore, is much more used than the above and consists of mixing cakes of neat cement, 3 ins. in diameter and $\frac{1}{2}$ in. thick, to the consistency shown by the ball test and observing when they will bear a needle $\frac{1}{12}$ in. in diameter weighted with $\frac{1}{4}$ pound. This is noted at the initial set. The final set is the time after which they will bear a needle $\frac{1}{24}$ in. in diameter weighted with 1 lb. In both cases the set is the time expressed in minutes between the mixing of the mortar and the failure of the needle to penetrate the surface. A good cement should not have its initial set in less than thirty minutes, or its final set in more than ten hours.

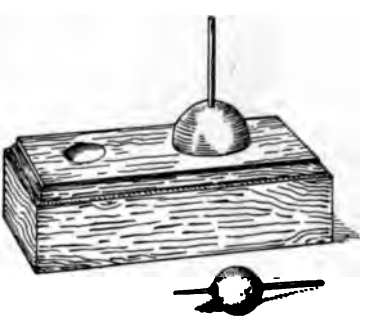


FIG. 95.—Gilmore Needles.

The U. S. Government specifications call for a minimum initial set of forty-five minutes.

Fig. 95 shows the Gilmore needles. The pats should be made with a flat top (so as not to catch the edge of the needle as shown in Fig. 96) and if made to taper towards the edge may be used for the soundness test also. They should

be kept in a moist closet or under a damp cloth to prevent drying out. A large covered tin box containing a wet sponge makes a good moist closet.

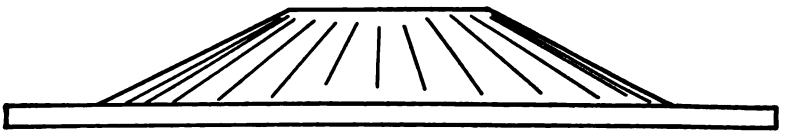


FIG. 96.—Pat for Determining Setting Time and Soundness.

Soundness or Constancy of Volume. For this test, which is intended to show the endurance of concrete made from the cement, pats about 3 ins. in diameter and ½ in. thick at the center, and tapering to a thin edge should be made upon a clean glass plate 4 ins. square. The paste from which the pats are made should be of normal consistency and they should be allowed to harden twenty-four hours in a moist closet. At the end of this time they should be exposed in an atmosphere of steam, above boiling water, in a loosely covered vessel for three hours. At the end of this time the pats should show no signs of cracking, distortion, or disintegration. Distortion has not taken place if

FIG. 97.—Appearance of Pats Made from Sound and Unsound Cement after Steaming.

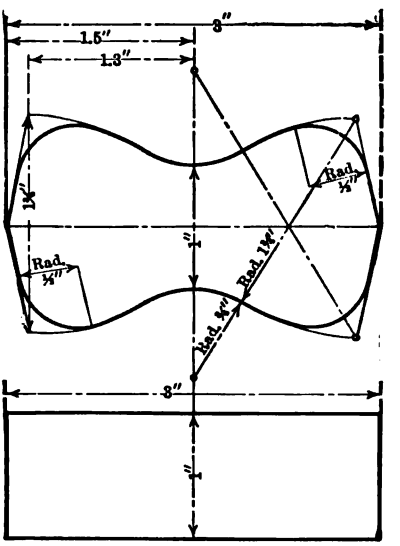
the pat sticks to the glass plate. Should it leave the plate, however, distortion may be detected by applying the edge of a ruler to the under side of the pat.

Fig. 97 shows six pats which have been steamed. Pats *E* and *F* have almost entirely disintegrated, while *B* is somewhat better and *A* and *D* almost sound. Pat *C* has stood the test successfully.

The cold-water test is also used (principally as a check upon the steam test) and consists in immersing a pat (similar to that used for steam) in cold water for twenty-eight days, at the end of which time it should show no signs of cracking, distortion, or disintegration.

The cracks due to disintegration should not be confused with those due to drying of the pat. The former are wedge shaped and radiate from the center of the pat, while the latter are usually running across the middle of the pat or around its edges. Shrinkage cracks due to drying are usually developed in a day or so, and are due to too thin (wet) a paste. Disintegration cracks rarely appear until after two or three days, and are due to expansives in the cement. The cracking of the glass to which the pat is attached during boiling means nothing to condemn the cement, and is due merely to unequal expansion of the pat and glass by the heat and a firm adhesion of the one to the other.

Where only a few tests have to be made, a convenient form of boiler consists of a tin bucket provided with a tin top. A few holes to permit exit of the steam are made in the top and a shelf of wire net or perforated tin is placed in the bucket. The pats are set on this and should be at least 2 ins. above the water.



DETAILS FOR BRIQUETTE.

FIG. 98.

Tensile Strength. The tensile strength of cement is tested both neat and with sand. In both tests the paste or mortar is moulded into a test-piece called a briquette, shown in Fig. 98, the least cross-section of which is 1 sq.in. in area. The moulds (Fig. 99) should be made of brass or bronze. They are made to permit of the making of but one briquette at a time (single moulds) or to permit of moulding a number of briquettes simultaneously (gang moulds).

The mortar is mixed just as described under the heading "Normal Consistency," about 125 grams of cement being used for each neat briquette, or 500 grams for a gang of four briquettes.

Immediately after mixing the mortar or paste, the moulds should be filled, the material pressed in firmly with the fingers and smoothed off with a trowel without ramming; the material should be heaped up on the upper surface of the mould, and, in smoothing off, the trowel should be drawn over the mould in such a manner as to exert a moderate pressure on the excess materials. The mould should be turned over and the operation repeated.

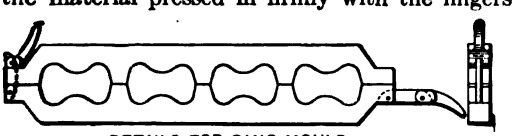

DETAILS FOR GANG MOULD.

FIG. 99.

The moulds containing the briquettes should then be kept in a moist closet, or under a damp cloth until the briquettes have hardened sufficiently to remove from the moulds, usually in about four to eight hours. On removal from the mould, the briquettes should be kept in the moist closet until they are twenty-four hours old, when, with the exception of the one-day briquettes, which are broken immediately, they should be placed in water, kept at as near 21° C. as possible.

The briquettes are then removed from the water at intervals and *immediately* broken by means of some form of testing machine. Fig. 100 shows the Fairbanks cement-testing machine. In this machine the briquette is held in the clips, *N* and *N*, and a stress is applied to it through the levers, *C* and *R*, by the weight of fine shot falling into the bucket, *F*. After the specimen breaks the stress required to rupture it is found by weighing the shot; the beam, *R*, being graduated for this purpose. In placing the briquette in the clips great care must be exercised to center it properly, as cross strains tend to lower the breaking strength. The briquettes must be broken as soon as they are removed from the water and the flow of shot into the bucket should be so regulated as to represent a load of about 600 lbs. per minute.

FIG. 100.
Fairbanks Cement-testing Machine.

Fig. 101 shows the Riehlé automatic cement-testing machine. This is a new type of machine which is coming into general use for cement testing, as it does away with some of the errors in the older form. In this type, the initial load is avoided by balancing a bucket of shot against a weight and the load is applied to the test specimen by allowing the shot to run out of the bucket. The load acting through the levers breaks the briquette when the shot is cut off by means of an automatic valve. The shot flowing out of the bucket are caught in a large cup resting on a spring scale which registers the load. This can be read as soon as the briquette breaks. The beam should be kept horizontal by means of the lever and worm gear as shown by the pointer on the beam.

Briquettes are usually broken in series from two to five each. The periods of breaking are after one day, seven days, twenty-eight days, three months, six months, one year, two years, three years, five years, ten years, etc. The tests of one year and upwards are usually called long-time tests. In some laboratories only one-day, seven-day and twenty-eight-day tests are made. The one-day briquettes are broken exactly twenty-four hours after they are made, the seven-day briquettes seven days after, etc.

Sand briquettes are made of a mixture of one part cement and three of standard sand, and these are first mixed dry and then the water is added and the moulding done as for neat briquettes. The standard sand at the present time is a natural sand from Ottawa, Ill., which is obtained from the Ottawa Silica Sand Co., Sandusky, O. It should be screened to pass a sieve made of wires 0.0165 in. in diameter and of 20 meshes to the linear inch and to be retained by a 30-mesh sieve (of 0.0112 in. diameter wire). Some testers, however, use crushed quartz, such as is used in the manufacture of sand-paper, sized to pass a No. 20 sieve and be retained on a No. 30. The Ottawa sand, however, gives the higher results. No sand briquettes are usually broken for twenty-four hour periods.

Both sets of specifications require a minimum strength of 500 lbs. neat, and 200 lbs. with sand after seven days, and 600 lbs. neat and 275 with sand after twenty-eight days, and also that the average figures in each case must be higher for the latter than for the former period.

Notes. After use, the moulds should be scraped free of hardened cement with a piece of soft metal (such as copper or zinc), brushed off with a stiff blacking brush, and wiped with a cloth and a little machine oil.

Neat briquettes should be marked with a stencil so as to identify them, and the sand briquettes placed in the water below the neat ones in such a manner as to identify the former. Usually the sand briquettes are placed edgewise in the water, and the corresponding neats are placed edgewise on top of the sand.

Small troughs or tanks consisting merely of galvanized iron pans, 3 ins. deep, may be purchased and will answer where only a few tests are to be made. Otherwise shallow wooden troughs lined with zinc will be found convenient. They may be placed one above the other.

FIG. 101.
Riehlé Automatic Cement-testing Machine.

Apparatus Needed for Cement Testing. The following apparatus will be needed for cement testing:

1. Apparatus for specific gravity, Le Chatelier's.
2. Scale for fineness.
3. Sieve—100 mesh, standard.
4. Sieve—200 mesh, standard.
5. Vicat apparatus (or Gilmore needles).
6. Trowel—8 ins.
7. Rubber gloves.
8. Measuring glass—500 cc. capacity.
9. Slab of glass (or brass), 24×24 ins.
10. Scale, capacity, 1000 grams.
11. Weights for above scale.
12. Glass plates—4×4 ins.
13. Moulds.
14. Testing machine.
15. Standard sand.
16. Galvanized iron pan, 24×24×13 ins.

STANDARD METHOD FOR CHEMICAL ANALYSIS OF PORTLAND CEMENT[1]

Solution

One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for fifteen minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cc. of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.[2] The solution is then evaporated to dryness, as far as this may be possible on the bath.

Silica (SiO_2)

The residue without further heating is treated at first with 5 to 10 cc. of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for ten minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue, without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for fifteen minutes and checked by a further blasting for ten minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. of HFl and 4 drops of H_2SO_4, and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.[3]

Alumina and Iron (Al_2O_3 and Fe_2O_3)

The filtrate, about 250 cc., from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 cc. of strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the

[1] Method Suggested for the Analysis of Limestones, Raw Mixtures, and Portland Cements by the Committee on Uniformity in Technical Analysis with the Advice of W. F. Hillebrand.

[2] If anything remains undecomposed it should be separated, fused with a little Na_2CO_3, dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

[3] For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation, never.

beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted five minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3+Fe_2O_3$.[1]

Iron (Fe_2O_3)

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water, the small amount of silica is filtered out, weighed and corrected by HFl and H_2SO_4.[2] The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing CO_2 through the flask, and titrated with permanganate.[3] The strength of the permanganate solution should not be greater than .0040 gram Fe_2O_3 per cc.

Lime (CaO)

To the combined filtrate from the $Al_2O_3+Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for twenty minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 cc. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al_2O_3 separates, this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed,[4] weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.[5]

Magnesia (MgO)

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam bath to about 150 cc., 10 cc. of saturated solution

[1] This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

[2] This correction of $Al_2O_3Fe_2O_3$ for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 milligrams of SiO_2 are still to be found with the $Al_2O_3Fe_2O_3$.

[3] In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

[4] The volume of wash-water should not be too large; *vide* W. F. Hildebrand.

[5] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium ortho-phosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to 100 cc., 1 cc. of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about two hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$. Portland cement must not contain more than 4% magnesia.

Alkalies (K_2O and Na_2O)

For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of $CaCO_3$ with NH_4Cl.

Anhydrous Sulphuric Acid (SO_3)

One gram of the substance is dissolved in 15 cc. of HCl, filtered and residue washed thoroughly.[1]

The solution is made up to 250 cc. in a beaker and boiled. To the boiling solution 10 cc. of a saturated solution of $BaCl_2$ are added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as $BaSO_4$. Both specifications require cement to contain not more than 1.75% SO_3.

Total Sulphur

One gram of the material is weighed out in a large platinum crucible and fused with Na_2CO_3 and a little KNO_3, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall, narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with HCl and made up to 250 cc. with distilled water, boiled, the sulphur precipitated as $BaSO_4$ and allowed to stand over night or for a few hours.

Loss on Ignition

Half a gram of cement is to be weighed out in a platinum crucible, placed in a hole in an asbestos board so that about three-fifths of the crucible projects below, and blasted fifteen minutes, preferably with an inclined flame. The loss by weight, which is checked by a second blasting of five minutes, is the loss on ignition. This must not be more than 4%.

[1] Evaporation to dryness is unnecessary, unless gelatinous silica should have separated, and should never be performed on a bath heated by gas; *vide* W. F. Hildebrand.

May, 1903: Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should, therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

Insoluble Residue

In addition to the above the U. S. Government specifications require the cement to show not more than 1% insoluble residue as determined below.

A 1-gram sample is digested on the steam bath in HCl of approximately 1.035 sp.gr. until the cement is dissolved. The residue is filtered, washed with hot water, and the filter paper and contents digested on the steam bath in a 5% solution of sodium carbonate. The residue is then filtered, washed with hot water, then with hot HCl (1.035 sp.gr.) and finally with hot water, then ignited at a red heat and weighed. The quantity so obtained is the insoluble residue.

RAPID METHOD FOR CHEMICAL ANALYSIS OF PORTLAND CEMENT [1]

Before submitting the cement to a chemical analysis it should be passed through a No. 100 test sieve to free it from pieces of clinker too large to be quickly attacked by the acid.

Weigh 0.5 gram of cement into a wide platinum or porcelain dish. The former is the more expensive of the two, but it is a better conductor of heat and there is no danger of contaminating the solution with silica, etc., from the dish, if the evaporation is conducted in platinum. The silica can also be entirely removed from a platinum dish. Now stir up the sample of cement in the dish with 10 cc. of cold water until all lumps are broken up, and add immediately 10 cc. of cold dilute hydrochloric acid (1 : 1). Place the dish on a water bath and evaporate to dryness, stirring occasionally. The water bath will evaporate as fast as anything else and there is no danger of the silica's spattering, which it is apt to do, unless the operation is very carefully watched, when a hot plate is used. As soon as the contents of the dish are dry, cool, add 10 cc. of dilute hydrochloric acid and 30 cc. of water, digest five or ten minutes on the hot plate, filter and wash ten times with hot water. Evaporate the filtrate to dryness. Cool, add 10 cc. of dilute hydrochloric acid and 50 cc. of water to the contents of the dish, cover with a watch-glass and digest on the hot plate for five or ten minutes. Filter off the slight residue of silica on a 9-cm. filter, wash well (seven to ten times) with hot water and put in a weighed platinum crucible together with the silica obtained from the first filtration. Ignite over the Bunsen burner until all the filter paper is consumed and then ignite strongly over a blast lamp for ten minutes. Cool in a desiccator and weigh as SiO_2; multiply the weight by 200 for per cent of silica, SiO_2.

Heat the filtrate to boiling and add a faint but distinct excess of ammonia. This can be most conveniently done by means of a bottle, fitted with a siphon tube, the end of which terminates in a jet, connected to it by a short piece of rubber tubing, which is closed by a pinch cock. The bottle stands on a shelf

[1] Method used in the laboratories of most cement companies and for routine work.

over the reagent table, and the siphon extends to within six inches of the surface of the table. The beaker is placed under the jet, and the ammonia can be very carefully and conveniently added by pressing the pinchcock. After adding the ammonia replace the beaker on the hot plate and boil for five minutes. Remove from the hot plate and allow the precipitate to settle. Filter onto an 11-cm. filter paper and wash once with hot water to collect the precipitate in the cone of the filter. Invert the funnel over the beaker in which the precipitation was made and wash practically all of the precipitate into this, allowing the filter to remain in the funnel. Dissolve the precipitate in 20 cc. of 10% nitric acid (1 : 10) and dilute the solution to 100 cc. Heat to boiling and reprecipitate with ammonia as before. Boil for five minutes, allow the precipitate to settle and filter through the same filter paper as used for the first precipitation. Wash once with hot water. Ignite carefully in a weighed crucible over a Bunsen burner and finally blast for five minutes. Cool and weigh as combined oxides of iron and alumina, $Fe_2O_3+Al_2O_3$. This precipitate also contains manganese dioxide, phosphoric and titanic acids, all of which are present in small quantities in the cement. Determine the iron oxide as directed further on, and deduct from the combined weights for the alumina, Al_2O_3 (phosphoric acid, titanic acid, etc.).

Make the filtrate from the iron and alumina alkaline with ammonia; boil and add 20 cc. of boiling saturated ammonium oxalate solution (or better, 3 grams of solid ammonium oxalate dissolved in 25–50 cc. of boiling water just prior to use). Stir well, allow fifteen minutes to settle, filter on an 11-cm. filter, and wash ten times with hot water, using as little as possible (about 100–125 cc.) to do the work well. Proceed as in A or B.

A. Gravimetric. Place the precipitate in a weighed platinum crucible, ignite, and weigh, after ignition over a blast-lamp to constant weight, as calcium oxide, CaO. Report as such.

B. Volumetric. Transfer the paper and precipitate to the beaker in which the latter was formed, and opening, spread it out against the upper side of the beaker. Wash the precipitate off the paper with a jet of hot water, fold the paper over, add 50 cc. of dilute (10%) sulphuric acid (1 : 10) to the contents of the beaker, dilute to 150 cc. and heat until the liquid is between 60 and 90° C. Titrate with permanganate solution until the pink color is produced. All this time the paper should be sticking to the walls of the beaker. Now drop this into the solution and stir. The pink color of the latter will be discharged. Finish the titration very carefully by adding permanganate, a drop at a time, and calculate the lime.

If the filtrate from the lime measures over 250 cc., acidify and evaporate until this bulk is reached. This can be rapidly done by using a large (8 in.) porcelain dish in the following manner: Place a piece of wire gauze on a tripod and in the center of this a round piece of thin asbestos paper about the size of a silver dollar. Now place the dish on this and a Bunsen burner turned fairly low under the asbestos dish. The contents of the dish can then be made to evaporate rapidly, without boiling, by regulating the flame. When the solution measures 250 cc., transfer to a beaker. If necessary, cool and, when perfectly cold, add 15 cc. of a 10% solution of sodium phosphate and 25 cc. of strong ammonia. Stir thoroughly and set aside in a cool place for at least six hours. Filter, wash with a mixture of water 800 cc., ammonia (0.96 sp.gr.) 200 cc., and ammonium nitrate 100 grams; place in a weighed platinum or porcelain crucible

and ignite over a low flame until all carbon is burned off. (Do not use the blast lamp.) Cool in a desiccator and weigh as magnesium pyrophosphate, which weight multiplied by 72.38 gives the percentage of magnesia, MgO.

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter [1] through a small filter, washing the residue well with water and catching the filtrate and washings in a small beaker. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, stannous chloride solution (25 grams in 100 cc. of dilute 1 : 3 hydrochloric acid) until the last drop makes the solution colorless. Add 3 drops in excess. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold, add 15 cc. of saturated mercuric chloride solution and stir the liquid with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in standard bichromate solution carefully from a burette until a drop of iron solution tested with a drop of 1% solution of potassium ferricyanide no longer shows a blue, but instead a yellow color. Multiply the number of cc. of bichromate used by the ferric oxide equivalent per cc. of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent of the ferric oxide in the cement. The most convenient strength for the standard bichromate solution is 3.074 grams of the salt to the liter. One cc. of this solution is equivalent to 0.005 gram ferric oxide. It should be standardized against iron wire or ferrous ammonium sulphate.

Weigh 1 gram of the sample into a small dry beaker and stir it up with 10 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 7.5 cc. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. Filter through a small paper and wash the residue thoroughly. Dilute the filtrate to 250 cc., heat to boiling, and add 10 cc. of boiling 10% barium chloride solution. Stir well and allow to stand overnight. Filter, ignite, and weigh as $BaSO_4$, which, multiplied by 34.29, gives the percentage of SO_3.

Place one-half gram of the cement in a clean platinum crucible which has been previously ignited to redness and cooled in a desiccator. Cover with the lid and weigh. Ignite for fifteen minutes over a good blast lamp. Rinse off the crucible lid with hot water to remove volatile salts condensed on the latter. Ignite the lid to redness and cool the crucible and lid in a desiccator. Weigh and the loss in weight multiplied by 200 is "loss on ignition."

For the alkalies in cement see analysis of clay.

[1] May be omitted if the cement practically all dissolves. Most cements do.

RAPID METHOD FOR CHECKING THE PERCENTAGE OF CALCIUM CARBONATE IN CEMENT MIXTURE

The following rapid method is generally used in the cement industry for checking the composition of the ground mixture of raw materials before these are fed into the kiln.

Standard Alkali

This should be exactly 2/5 normal and may be prepared in any convenient manner. Usually 8 or 10 liters are made up at one time and kept in a bottle provided with a siphon tube and with a layer of coal oil on top of the solution about ½ in. thick to prevent the absorption of carbon dioxide by the caustic soda.

Phenolphthalein should be used as an indicator. A 1% solution of this is employed.

One cc. of 2/5 N alkali is equivalent to exactly 0.02 gram of $CaCO_3$ or to 2% where 1-gram sample is used.

Standard Acid

Take the specific gravity of a bottle of hydrochloric acid, using a hydrometer for the purpose. Refer to a table of specific gravities of hydrochloric acid and calculate from this the quantity of acid necessary to contain 97.0 grams of HCl.

Measure this quantity of the acid into a liter flask and dilute to the mark, pour into an 8-liter bottle and add 7 liters of water, measuring with the flask. Mix the contents of the bottle well by shaking. Ten cc. of this solution should be equivalent to from 8.1 to 8.5 cc. of the 2/5 N alkali when checked by adding a drop of phenolphthalein solution and running in the alkali to a purple red color. If its value does not lie between these figures add acid or water to make it of this strength.

Standard Sample

A standard sample of raw material is necessary to standardize the acid and alkali for actual use. This sample should be ground in the same manner as the daily run of samples to be checked by the acid and alkali. It should all pass a 100-mesh sieve and be freed from hygroscopic moisture, by drying for some hours, at 110° C. Three or four pounds of this sample should be prepared and kept in air-tight jars or bottles. A small sample (1 or 2 oz.) of this should be placed in a 2-oz. bottle and stoppered with a rubber cork when not in use. This small sample can then be redried for an hour at 100–110° C. and used for standardizing, avoiding the frequent opening and mixing of the contents of the large jars or bottles.

After drying, the standard sample should be carefully analyzed. It should contain approximately the quantity of carbonate of lime which it is desired to have in the mix, and the amount of magnesia should also be normal. When the magnesia varies at different times, fresh standard samples should be prepared to contain these varying percentages of magnesia; otherwise the lime will be reported incorrectly.

Standardizing the Acid

Weigh 1 gram of the standard sample into a 600-cc. Erlenmeyer flask and run in from a pipette 50 cc. of standard acid. Close the flask with a rubber stopper, having inserted through it a long glass tube 30 ins. long and about $\frac{3}{8}$ in. internal diameter. Heat the flask on a wire gauze over a burner as shown in Fig. 102 until steam *just begins* to escape from the upper end of the tube. The heating should be so regulated that the operation requires very nearly two minutes, from the time the heat applied, until steam issues from the tube. Remove the flask from the heat, as soon as the steam escapes from the tube, and rinse the tube into the flask, in the following manner. Rest the flask, still stoppered, on the table and grasp the tube between the thumb and forefinger of the left hand. Direct a stream of cold water, from a wash-bottle in the right hand, down the tube, holding the latter inclined at an angle of 45°, and rolling the flask from side to side on the table, in sweeps of 2 or 3 ft., by twirling the tube between the finger and thumb. Unstopper the flask and rinse off the sides and bottom of the stopper, into the flask, and wash down the sides of the latter. Add a drop or two of phenolphthalein and run in the standard alkali, from a burette, until the color changes to purple red. This color is often obscured until the organic matter settles, so it is necessary to hold the flask to the light and observe the change by glancing across the surface. A little practice will easily enable the operator to carry on the titration with accuracy and precision.

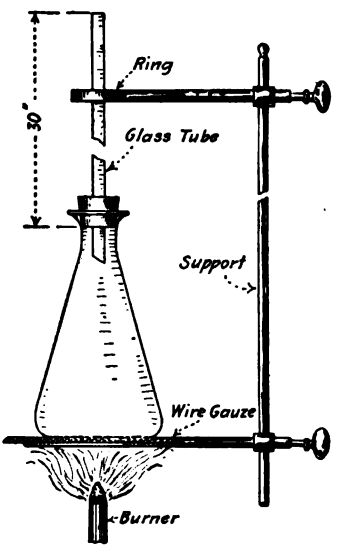


FIG. 102.—Apparatus for Determining Calcium Carbonate with Acid and Alkali.

If the standard sample contains L per cent carbonate of lime and d cc. of alkali are required to produce the purple red color, then, to find the carbonate of lime in other samples it is only necessary to subtract the number of cc. of alkali required in their case from d, multiply the difference by 2, and add to L for the percentage of carbonate of lime in them; or the number of cc. is greater than d, subtract d from this number, multiply by 2, and subtract from L for the carbonate of lime.

In order to avoid all calculations, prepare a table giving the various percentages of carbonate of lime corresponding to different quantities of alkali.

Determination

Weigh 1 gram of the sample, which has been ground to pass a 100-mesh sieve, into the flask, add 50 cc. of the standard acid and proceed as directed under standardizing the acid. The percentage of carbonate of lime may be found from the number of cc. of alkali used either from the preceding table or by the formula

$$\text{Per cent } CaCO_3 = L + (d - S) \times 2,$$

where L and d have the same values as in the paragraph on "Standardizing the Acid" and S represents the number of cc. required for the sample whose composition is desired.

ANALYSIS OF LIMESTONE, CEMENT ROCK, LIME, ROSENDALE CEMENT, ETC.

Dr. Porter W. Shimer, of Easton, Pa., modifies the standard limestone scheme by fusing the sample with half its weight of sodium carbonate. By this means the silicates are decomposed, and yet the quantity of sodium carbonate introduced into the solution is so small that the lime and magnesia precipitates are not contaminated with sodium salts. Below is the method.

Silica, etc. Mix thoroughly 0.5 gram of the finely ground sample with ½ gram of sodium carbonate. Place over a low flame for a few minutes, then gradually raise the flame. Heat over the full flame for five minutes and then over the blast lamp for five minutes. There will be no complete fusion, only a sintering. Put the crucible in a small beaker or casserole and add 30 cc. of water and 10 cc. of hydrochloric acid (sp.gr. 1.10). When the mass is dissolved out of the crucible, rinse the latter off into the beaker and remove any adhering matter with a rubber-tipped rod. To the solution in the beaker or casserole add a little bromine water or a few drops of nitric acid, evaporate to dryness and proceed as directed in the analysis of Portland cement.

For loss on ignition, weigh into a tared platinum crucible 0.5 gram of the sample. Heat at first over a low flame, then gradually raise the temperature and finally ignite over a blast lamp until it ceases to lose weight on reheating. Report such loss in weight as "loss on ignition."

To determine iron and alumina separately, fuse the precipitated ferric oxide and alumina with caustic potash in a silver crucible or dish. Treat with water, boil, and filter. Ignite the residue after washing and weigh as ferric oxide. This weight subtracted from the combined weight of the ferric oxide and alumina gives the weight of the alumina, Al_2O_3.

To determine alkalies in limestone use the method described for clay, employing 8 grams of the sample and 1 gram of ammonium chloride, but no calcium carbonate.

ANALYSIS OF ALLOYS[1]

JOHN C. OLSEN[2]

Difficulty of Complete Separation of Elements. As the great majority of the substances with which the chemist is called upon to deal are complex rather than simple, a careful study of the separation of the elements is of the greatest importance. Only by the closest attention to details can success be attained in the analysis of complex substances. The importance of testing precipitates for impurities and the solution for unprecipitated portions of an element cannot be too strongly urged. Only in this manner can the accuracy of an analysis be assured.

Limit of Accuracy in Analysis. If a complete analysis is made the sum of all the constituents must be very close to 100%. A summation which is within .5% can generally be obtained if the analysis is conducted with care and reliable methods are used. In general the analysis of an unknown substance should be conducted in duplicate. If the duplicate results do not agree within .2 or at most .3%, a third analysis should be made. As the error of most determinations is at least .1%, it is unnecessary to calculate results to more than hundredths of per cent. As the error in each determination of the analysis of a given substance may be either plus or minus, the practice of dividing the difference between the summation and 100% among the various determinations is not justifiable.

It is in some cases possible to analyze a substance in such a manner that the results are accurate to the hundredth of a per cent. Such results may be computed to the .001 of a per cent. This practice is common in the analysis of metals. Large quantities of the metal are taken, so that considerable quantities of the impurities which are present in small amounts are obtained for determination. The results may then be accurate to the hundredth of a per cent. This does not imply a higher degree of accuracy in the determination of a given element than .1 of a per cent. For example, if iron were present in copper to the extent of .5%, a determination of the iron which is accurate to .01% of the impure copper would represent an error of $\frac{1}{50}$ of the amount of iron present in the copper. In giving the results of such analyses the percentage of the main constituent is obtained by difference, so that the summation is exactly 100%.

Analysis of Type Metal

Alloy of Copper, Lead, Antimony, Tin, with Small Amounts of Iron and Arsenic

Solution of the Alloy. To 1 gram of the alloy, which has been cut into small shavings with a clean knife, or sampled by means of a clean hack-saw producing fine "sawings," are added 15 cc. concentrated hydrochloric acid. The solution

[1] "Quantitative Chemical Analysis," 5th Ed, by J. C. Olsen. D. Van Nostrand Company, Publishers.

[2] Professor in charge of Department of Chemistry, Cooper Union, New York City.

is gently warmed on the water bath and a drop or two of concentrated nitric acid is added occasionally until solution is effected. All of the metals will be converted into chlorides which will remain in solution with the possible exception of lead chloride. An excess of nitric acid is to be avoided, as it tends to form insoluble metastannic acid, which can be readily distinguished from the crystalline lead chloride. If metastannic acid forms, the operation must be repeated, using less nitric acid or adding it less frequently. After a few trials the correct method of adding the nitric acid is soon acquired.

Lead. The solution is allowed to cool and then stand at least one-half hour or better overnight to allow the lead chloride to crystallize out. Ten times the volume of absolute alcohol is then added in several portions. After standing for about half an hour, the lead chloride is filtered off on a Gooch crucible, washed with a mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid, and finally with pure alcohol. It is dried for three hours at 150° and weighed. The great advantage of this method of separating the lead is that the very troublesome treatment of the sulphides of the metals present with sodium or potassium sulphide is avoided. The *most difficult part* of the operation is the solution of the alloy.

Copper and Iron. The filtrate from the lead chloride is heated until the alcohol is expelled. Two grams of tartaric acid and an excess of ammonia are added and the solution warmed until the precipitate dissolves. By the addition of 5 cc. of saturated hydrogen-sulphide water, the copper and the small amount of lead still unprecipitated as well as a trace of iron which may be present may be precipitated without bringing down any of the tin and antimony. The solution is warmed and when the dark-colored precipitate has settled, 1 cc. of the hydrogen-sulphide water is added to the clear supernatant liquid. If no further precipitate is produced, the solution is filtered and the precipitate washed with water containing hydrogen sulphide.

The precipitate is dissolved in a little warm dilute nitric acid and the lead separated as sulphate, the nitric acid being expelled by evaporation after the addition of sulphuric acid. The copper is precipitated from the filtrate as sulphide and if small in amount may be ignited and weighed as oxide. If considerable copper is present it must be weighed as sulphide or without precipitation as sulphide may be separated electrolytically from the iron. One or 2 cc. concentrated nitric acid are added and a current of one-half ampere passed until all the copper is precipitated. The iron may then be precipitated with ammonia and weighed as oxide.

Separation of Antimony and Tin. The solution of antimony and tin is acidified with hydrochloric acid, hydrogen sulphide passed, and the precipitate filtered off and washed two or three times. A hole is made in the point of the filter-paper by means of a glass rod and the bulk of the precipitate washed into a beaker with a little water. Warm dilute hydrochloric acid is poured over the paper to dissolve the portion of the precipitate still adhering to the paper. The precipitate in the beaker is dissolved by warming and adding concentrated hydrochloric acid. The hydrogen sulphide is decomposed by the addition of a crystal of potassium chlorate and warming. Some pure metallic iron is added and the solution heated on the water bath for about one-half hour or until the iron is nearly dissolved. The precipitated antimony is filtered off on a Gooch crucible, a little iron having been sprinkled on the asbestos. The precipitate is washed with boiled water to which considerable hydrochloric acid has been added.

The antimony is dissolved in hydrochloric acid to which a little potassium chlorate has been added. The solution is warmed to expel chlorine and, after the addition of tartaric acid and water, hydrogen sulphide is passed. The antimony sulphide is filtered off and washed with water containing a little hydrogen sulphide. The moist precipitate is rinsed into a capacious porcelain crucible with water. The small portion still adhering to the paper is dissolved in a little warm ammonium sulphide and the solution allowed to flow into the crucible. The solution is evaporated on the water bath after the addition of a few cc. of concentrated nitric acid. If sulphur separates, a little liquid bromine is added when the solution has become quite concentrated. When the globule of sulphur has disappeared, expel the excess of nitric acid by heating on the hot plate or with the Bunsen burner, finally heating to full redness. Cool a little, sprinkle some ammonium carbonate over the precipitate, and ignite again to completely expel sulphuric acid and weigh as antimony tetroxide, Sb_2O_4.

The antimony may also be weighed as the trisulphide, Sb_2S_3. The precipitate is filtered on a weighed Gooch crucible, and heated to 230° in a stream of carbon dioxide to exclude oxygen until constant.

Tin. To precipitate the tin in the filtrate from the antimony the excess of hydrochloric acid is neutralized with ammonia, the solution diluted somewhat, warmed, and hydrogen sulphide passed until the tin is entirely precipitated. The stannous sulphide is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is dried and detached from the paper which is burned. The precipitate and the ash are placed in a weighed porcelain crucible and heated very gently with free access of air until sulphur dioxide ceases to be given off. The oxidation may be assisted by the addition of a few drops of nitric acid. Finally the precipitate is strongly heated to expel sulphuric acid, which is completely removed by the addition of a little ammonium carbonate and again igniting. It is weighed as stannic oxide, SnO_2.

Arsenic. As only a trace of arsenic is present, a 5- or 10-gram portion of the alloy should be taken for its determination. Dissolve in hydrochloric acid and potassium chlorate and warm to expel the chlorine. Filter off the lead chloride on asbestos and wash a few times with dilute hydrochloric acid. Add one-third the volume of concentrated hydrochloric acid and pass hydrogen sulphide. Filter off the precipitate consisting of the sulphides of copper and arsenic on asbestos, wash with hot water containing hydrogen sulphide and a little hydrochloric acid. Dissolve the arsenic sulphide by washing the precipitate with a little warm dilute ammonia. Evaporate the solution nearly to dryness in a porcelain dish. Oxidize the arsenic by warming with concentrated nitric acid, dilute the solution somewhat, neutralize with filtered ammonia, and add magnesia mixture. After standing twenty-four hours filter, wash, ignite, and weigh as magnesium pyroarsenate according to the directions given in chapter on Arsenic.

Analysis of Soft Solder

Alloy of Lead and Tin, Generally Containing Small Amounts of Arsenic, Antimony, Iron, and Zinc

Solution of the Alloy. One gram of the alloy is weighed out and transferred to a beaker of about 500-cc. capacity. Ten cc. of concentrated nitric acid and 5 cc. of water are added. The beaker is covered with a watch-crystal and heated

on the water bath until the alloy is completely decomposed and the nitrous fumes are entirely expelled. One hundred cc. of water are added and the solution boiled for five minutes and allowed to settle for one hour. The stannic oxide is filtered off and washed with hot water. The moist precipitate may be introduced into a weighed porcelain crucible, the paper burned in the usual manner, and finally heated to redness for ten minutes.

Tin. When the precipitate has been brought to constant weight, it is fused with six times its weight of a mixture of equal parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The insoluble sulphides are washed with hot water and treated with a little dilute hydrochloric acid and the paper washed with water. If ***copper*** is present it will remain on the paper and the small amount present may be weighed as CuO after burning the paper in a porcelain crucible and igniting the precipitate. The lead is precipitated by the addition of a few drops of sulphuric acid and 25 cc. of alcohol to the solution, which should not exceed 50 cc. After standing one hour, the precipitate is filtered off on a Gooch crucible, washed with alcohol, dried on the hot plate, and weighed. The filtrate is evaporated until the alcohol is completely expelled. Any iron present is precipitated with ammonia and weighed. Hydrogen sulphide is passed through the filtrate to precipitate any zinc present, which is filtered off. The filtrate from the insoluble sulphides will contain the tin as a thiostannate and part of the ***antimony*** present in the alloy as a thioantimonate. The solution is boiled after the addition of caustic soda and hydrogen peroxide until it is nearly decolorized. On acidifying and passing hydrogen sulphide both metals are precipitated as sulphides. If antimony is present the metals should be separated by the method given under Analysis of Type Metal, page 660. The weight of the impurities found, computed as oxides, is deducted from the weight of the impure stannic oxide.

Lead. The filtrate from the stannic oxide is transferred to a porcelain dish, 5 cc. concentrated sulphuric acid added, and evaporated until fumes of sulphuric acid are evolved. Cool the dish by floating it in cold water and add cautiously 75 cc. of water. Stir thoroughly and add 25 cc. of alcohol. Allow the solution to stand for at least one hour, filter off the lead sulphate on a weighed Gooch crucible, wash with alcohol until free from acid, dry on the hot plate, and weigh.

Arsenic and Antimony. The alcohol is completely expelled from the filtrate by evaporation and any arsenic present precipitated by passing hydrogen sulphide. If this precipitate is of an orange color instead of pure yellow, antimony is present. It should be filtered off and washed with water containing a little hydrochloric acid until free from iron and hydrogen sulphide. It is then washed with small portions of concentrated ammonium carbonate solution until the arsenic sulphide is entirely dissolved. The arsenic is reprecipitated by acidifying the solution with hydrochloric acid and passing hydrogen sulphide. It is filtered off on a Gooch crucible and washed with water containing hydrogen sulphide and a little hydrochloric acid. The water is removed by alcohol and the precipitate digested with carbon disulphide until sulphur is entirely removed. The arsenic sulphide is dried at 100° and weighed. If antimony is absent the treatment with ammonium carbonate is omitted, the precipitate being filtered off on a Gooch crucible, washed, dried, and weighed. If antimony is present it is ignited and weighed as directed in page 660 under the Analysis of Type Metal.

Iron. A few drops of bromine water are added and the solution is boiled to oxidize the iron and to expel the hydrogen sulphide. The iron is then precipitated by

making the filtrate alkaline with filtered ammonia and warming for a few minutes. It is filtered off on a small paper and dissolved by adding a few drops of dilute hydrochloric acid. The paper is washed with about 75 cc. of water in small portions. The iron is reprecipitated and filtered on the same paper after moistening with a few drops of ammonia. After washing free from chlorides, the moist paper is transferred to the weighed platinum crucible and ignited.

Zinc. Hydrogen sulphide is passed into the combined filtrates to precipitate any zinc present, which is filtered off, washed, and weighed as sulphide after ignition with sulphur in a stream of hydrogen.

Analysis of Rose's Metal

Alloy of Lead, Bismuth, and Tin, Generally Containing Small Amounts of Copper, Arsenic, Antimony, Iron and Zinc

One gram of the metal is weighed out and decomposed with nitric acid and the ***stannic oxide*** is weighed, according to the procedure under analysis of soft solder, page 662.

Lead. To the filtrate from the stannic oxide containing the nitrates of lead and bismuth, 5 cc. concentrated sulphuric acid are added. The solution is evaporated in a porcelain dish until sulphuric-acid fumes are given off. The dish may be placed on the hot plate, sand bath, or wire gauze and the liquid heated to just below the boiling-point to avoid spattering. When the acid becomes concentrated, the heat may be somewhat increased. The hot concentrated solution is diluted by slowly pouring it with constant stirring into about 100 cc. of water and digested hot for about half an hour with occasional stirring. The lead sulphate is then filtered off on a Gooch crucible, washed with 10% sulphuric acid until the wash-water no longer gives a precipitate on making it alkaline with ammonia, adding ammonium carbonate, and warming. The sulphuric acid is then washed out with alcohol. The precipitate is dried and weighed. It is tested for a possible contamination with bismuth as follows: It is dissolved in 5 to 10 cc. of warm concentrated hydrochloric acid and 50 cc. of absolute alcohol are added to the solution. After standing for a few moments, the solution, containing the bismuth as chloride, is filtered off. By nearly neutralizing with ammonia, and largely diluting with water, the bismuth is precipitated as oxychloride and may be washed with water containing a few drops of hydrochloric acid, dried, and weighed.

Bismuth. In the filtrate from the lead sulphate, the bismuth is precipitated by just neutralizing with filtered ammonia, adding a few drops of ammonium carbonate and warming the solution gently for about fifteen minutes. The precipitate is filtered off and washed a few times with water. To free the precipitate from a small amount of basic sulphate it is dissolved in a small amount of dilute nitric acid and reprecipitated. The precipitate is washed with water containing a little ammonium nitrate and dried. It is removed from the paper as completely as possible and placed on a watch-crystal. The paper is replaced in the funnel, moistened with a few drops of dilute nitric acid, and washed with small amounts of warm water. The wash-water is evaporated to dryness in a fairly large weighed porcelain crucible, and the residue ignited until the nitric acid is completely expelled. The main portion of the precipitate is now added, heated with the Bunsen burner and weighed as Bi_2O_3.

Copper. If copper is present in the alloy, it will be contained in the two

filtrates from the bismuth precipitate. Combine these filtrates, acidify with hydrochloric acid, and concentrate to a convenient bulk. Pass hydrogen sulphide through the warm solution, filter, and wash with water containing hydrogen sulphide. Even if copper is absent, a small black precipitate of bismuth sulphide will be obtained at this point because of the slight solubility of the bismuth hydroxide or carbonate. The precipitate may be tested for bismuth by treating with a little dilute hydrochloric acid and diluting the filtrate. A white precipitate indicates bismuth. The copper sulphide, being insoluble in dilute hydrochloric acid, remains on the paper and may be ignited together with the paper and weighed as oxide. If ***arsenic, antimony, iron*** or ***zinc*** are present they are separated and determined by the methods given under Analysis of Type Metal, page 664.

Analysis of Wood's Metal

Alloy of Lead, Bismuth, Tin, and Cadmium, Generally Containing Small Amounts of Copper, Arsenic, Antimony, Iron and Zinc

One gram of the metal is weighed, dissolved in nitric acid, and the ***stannic oxide*** weighed and purified. The filtrate from the tin is evaporated to dryness on a water bath. The nitrates are converted into chlorides by evaporating twice on the water bath to a small bulk after the addition of 20 cc. of concentrated hydrochloric acid.

Lead. After cooling, 25 cc. absolute alcohol are added. The mixture is stirred and after standing some time the chloride of lead is filtered off on a Gooch crucible, and washed with an ice-cold mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid. It is dried on the hot plate or at 150° for three hours and weighed.

Bismuth. The filtrate is diluted with about one-half liter of water and nearly neutralized with ammonia (about 40 cc. of dilute ammonia will be required). After standing twenty-four hours the bismuth oxychloride is filtered off on a Gooch crucible, washed with water containing a few drops of dilute hydrochloric acid, dried at 110°, and weighed as BiOCl.

The bismuth may also be precipitated as bismuth hydroxide by volatilizing most of the alcohol, neutralizing with ammonia and warming gently. If ***iron*** is present this precipitate will be reddish. In that case it is best to dissolve it in hydrochloric acid and precipitate the bismuth as oxychloride. The bismuth hydroxide is ignited and weighed as oxide, Bi_2O_3.

Cadmium. The filtrate from the bismuth oxychloride is evaporated to a bulk of 200 or 300 cc. If the bismuth has been precipitated by means of ammonia, the filtrate is first acidified with hydrochloric acid and evaporated to a moderate bulk. The solution is saturated with hydrogen sulphide and the precipitate filtered off and washed with water containing hydrogen sulphide. If the cadmium sulphide is dark colored or black, traces of lead or bismuth sulphides may be present because of incomplete separations, or copper may have been present in the alloy. Any arsenic which may have been in the alloy or a trace of tin or antimony will also be present in this precipitate.

Arsenic, Antimony, and Tin. It should be tested for these three elements by pouring over it a few drops of warm potassium or sodium sulphide and washing two or three times with warm water, being careful to stir up the precipitate with the stream of water from the wash-bottle. A precipitate formed on acidifying the

filtrate indicates the presence of arsenic, antimony, or tin. If the characteristic orange color of antimony is absent, the supernatant liquid should be decanted and the precipitate warmed with a little concentated hydrochloric acid. If it dissolves completely, arsenic is absent and the tin may be reprecipitated by diluting and passing hydrogen sulphide. After washing, the moist precipitate with the paper may be burned and the sulphide of tin converted into oxide by ignition. If arsenic or antimony is present, it may be determined as directed in the Analysis of Type Metal, page 660.

Separation of Copper and Cadmium. To dissolve out any copper which may be present with the cadmium sulphide, a few drops of potassium cyanide should be poured over the precipitate. It should be thoroughly stirred up with water and washed a few times. If a considerable amount of copper is present, the bulk of the precipitate should be transferred to a beaker by washing out the paper while still in the funnel with a stream of water. The remainder of the precipitate on the paper is dissolved by washing with a little warm dilute nitric acid. The paper is then thoroughly washed with small portions of hot water. The washings are allowed to flow into the beaker containing the main portion of the precipitate. The beaker is warmed and more nitric acid is added if necessary to dissolve the precipitate. The solution is neutralized with sodium carbonate and a slight excess of potassium cyanide added. A small white precipitate at this point may be lead or bismuth carbonates, which should be filtered off and determined. On passing hydrogen sulphide through the filtrate, the cadmium is precipitated as sulphide and may be filtered off on a Gooch crucible and washed with water containing a little hydrogen sulphide. It is finally washed with pure water and the free sulphur extracted by washing with alcohol and then with carbon disulphide. The precipitate is dried at 100° and weighed.

Copper. The filtrate from the cadmium sulphide contains the copper and is acidified [1] with sulphuric acid and a little nitric acid and evaporated to fumes. The residue is dissolved in water, filtered if necessary, and the copper precipitated as sulphide. If it is small in amount it may be ignited and weighed as oxide. If considerable copper is present, it must be ignited with sulphur in a stream of hydrogen and weighed as cuprous sulphide, Cu_2S. When much copper is present, it is better to determine it electrolytically.

Separation of Iron and Zinc. The filtrate from the first precipitation with hydrogen sulphide contains any zinc or iron which may have been present. These metals may be separated in the following manner:

The solution is boiled to expel hydrogen sulphide, neutralized with ammonia, and acidified with acetic acid. Hydrogen sulphide is passed for some time and the solution allowed to stand for several hours. The clear liquid is carefully decanted through a filter paper, and after replacing the beaker containing the clear filtrate with another beaker, the sulphide of zinc is brought on the paper and washed with water containing ammonium acetate and acetic acid. The precipitate is dissolved in a little dilute nitric acid and the paper washed with hot water. The solution of the zinc is evaporated to dryness in a weighed porcelain crucible, ignited finally over the blast-lamp to decompose any zinc sulphate which may have been formed, and weighed as oxide. The filtrate is boiled to expel the hydrogen sulphide. A little nitric acid is then added to oxidize the iron, which is precipitated with

[1] This should be done under a hood with good draught to avoid any possibility of inhaling the very poisonous hydrocyanic-acid fumes.

ammonia and weighed as oxide. A very convenient method of oxidizing the iron and removing the hydrogen sulphide is by the use of bromine water. The bromine should be added until the solution is colored, indicating complete oxidation of the iron and the presence of an excess of bromine. If a solution of bromine in concentrated hydrochloric acid is used a few drops will suffice and the solution will not be diluted to any extent. If manganese is to be removed together with iron, the presence of an excess of bromine is advantageous; otherwise it must be boiled out. As the bromine oxidizes hydrogen sulphide in the cold, the excess of the latter need not be boiled out.

Analysis of Britannia Metal

Alloy of Tin, Antimony, and Copper, with Small Amounts of Bismuth, Lead, and Iron

Decomposition of the Alloy by Means of Chlorine. Alloys containing a large percentage of tin are best decomposed by a stream of chlorine. The method is applicable to alloys containing less than 15% of lead and copper.

A hard-glass combustion-tube 70 cm. long is taken and one end drawn out, making a small tube 20 cm. long, which is bent at right angles. This small tube is connected by means of a cork stopper with a Peligot tube the bulbs of which are nearly filled with dilute hydrochloric acid (1 : 3) containing about 1 gram of tartaric acid. A second Peligot tube is connected with the first and contains a solution of caustic soda (1 : 3). The chlorine is evolved in a 2-liter flask containing pieces of pyrolusite, over which concentrated hydrochloric acid is poured. The flask is heated on a water bath. The chlorine is passed through a wash-bottle containing water and then through two wash-bottles containing sulphuric acid. It is then passed into the combustion-tube, connection being made by means of a cork stopper. Wherever rubber is used for making connections, it must be well coated with paraffin. This is also advisable for the cork stoppers. The chlorine is not allowed to pass into the combustion-tube until all of the air has been displaced from the flask and the wash-bottles. All escaping chlorine should be absorbed in caustic-soda solution.

One gram of the alloy in *fine* turnings is weighed out and placed in a porcelain boat which is placed in the middle of the combustion-tube. The chlorine is first allowed to act on the alloy in the cold. When no further action is observed, the part of the tube in which the boat is situated is heated gently with the Bunsen burner, and then more strongly until the contents of the boat fuse. The ***chlorides*** of ***mercury, bismuth, arsenic, antimony,*** and ***tin volatilize*** and are driven out of the tube by heating it gently from the boat to the end which is drawn out. These chlorides are absorbed in the hydrochloric acid contained in the first Peligot tube, while the excess of chlorine is absorbed in the caustic-soda solution contained in the second Peligot tube.

The chlorine in the apparatus is then displaced by means of a stream of dry air or carbon dioxide, the chlorine generator having been removed. The apparatus is disconnected, the boat containing the ***chlorides*** of ***copper, lead,*** and ***iron*** is placed in a porcelain dish, and the tube washed out with hot water which is allowed to flow into the dish containing the boat. Hydrochloric acid is added and the dish warmed until the contents of the boat are dissolved. The latter is removed and washed.

Lead, Copper, and Iron. The lead is precipitated by evaporation with sulphuric acid and diluting and is filtered off and weighed as sulphate. The copper is precipitated by means of hydrogen sulphide and weighed as sulphide or determined electrolytically from a nitric acid solution. The iron is precipitated by means of ammonia and weighed as oxide.

The contents of the first Peligot tube are poured into a beaker and the Peligot tube well washed out with water to which hydrochloric acid is added if necessary. The solution is warmed and hydrogen sulphide passed until precipitation is complete. The filtrate should be heated to boiling, strong hydrochloric acid added, and hydrogen sulphide passed again to insure complete precipitation of the arsenic.

Bismuth. If the sulphide precipitate is dark colored, bismuth is present. The precipitate is washed into a beaker, ammonium sulphide added, and the solution warmed. The solution is filtered through the same paper and the precipitate washed with warm water containing a little ammonium sulphide. The bismuth sulphide is dissolved in a little warm dilute nitric acid and the paper washed. The bismuth is precipitated with ammonia and ammonium carbonate, ignited, and weighed as oxide, Bi_2O_3.

Separation of Tin from Arsenic and Antimony. The ammonium-sulphide solution of arsenic, antimony, and tin is poured with vigorous stirring into a hot solution of 25 grams of oxalic acid in 200 cc. of water. The solution is heated to boiling and hydrogen sulphide passed for about fifteen minutes. The precipitate is filtered off immediately and washed with hot water containing hydrogen sulphide. It is dissolved in ammonium sulphide and the treatment with hot oxalic acid and hydrogen sulphide repeated.

Tin. The oxalic-acid solution of tin is evaporated down, with the addition of 5 cc. concentrated sulphuric acid, to fumes. The solution is cooled, cautiously diluted with water, and hydrogen sulphide passed to insure complete precipitation of the tin. Wash the precipitate with water containing ammonium acetate and a little acetic acid, dry, ignite, and weigh as stannic oxide, SnO_2.

Arsenic and Antimony. The precipitate of arsenic and antimony sulphides is treated with a little concentrated ammonium-carbonate solution and washed to remove arsenic. The antimony is then weighed as oxide according to the directions given under the Analysis of Type Metal, page 660. The arsenic is determined according to the directions given in the same section.

Analysis of Brass or Bronze

Alloy of Lead, Copper, Tin, and Zinc, Small Amounts of Arsenic and Iron.

Solution of the Alloy. Weigh out 1 gram of the alloy and place in a 300-cc. beaker, add 10 cc. concentrated nitric acid and 5 cc. water. Cover the beaker with a watch-crystal and place in a dish of cold water. After one-half hour place the beaker on the water bath and evaporate the solution to dryness. One hundred cc. of boiling water and a few drops of nitric acid are added and the solution boiled for five minutes.

Tin. The stannic oxide is filtered off and washed with hot water. The moist precipitate is introduced into a weighed porcelain crucible and the paper burned in the usual manner. If the amount of tin is small (less than 1%) it is weighed at this point, otherwise it is fused with six times its weight of a mixture of equal

parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The *copper, lead,* and *iron* which were carried down with the stannic oxide will remain on the paper as sulphides, while the filtrate will contain all of the tin and any *arsenic* or *antimony* which may have been present. The insoluble sulphides are dissolved in a little nitric acid, the paper washed, and the solution added to the filtrate from the stannic oxide.

If arsenic and antimony are absent, the tin may be precipitated out of the sodium sulphide solution and weighed. The excess of sulphur should first be removed from the solution by heating to boiling after the addition of caustic soda and then adding hydrogen peroxide in small quantities until the solution is nearly decolorized. It is then acidified with hydrochloric acid while stirring constantly, heated, and hydrogen sulphide passed. The stannic sulphide is washed with hot water containing ammonium acetate and a little acetic acid. It is ignited and weighed as stannic oxide in the usual manner.

Arsenic and Antimony. If arsenic is present in the alloy, a small amount of this element will be present in the sodium sulphide solution of the tin and will be precipitated with the stannic sulphide. It may be removed by treating the precipitate with a little concentrated solution of ammonium carbonate and washing. The solution of arsenic should be added to the nitric acid solution of the alloy.

If antimony is also present in the alloy, the sulphides of arsenic, antimony, and tin must be separated by one of the methods given under Analysis of Type Metal, page 660.

Lead. To filtrate from the stannic oxide 5 cc. concentrated sulphuric acid are added and the solution evaporated in a porcelain dish until the nitric acid is entirely expelled and white fumes of sulphuric acid are given off. The solution is cooled by floating the dish on cold water and diluted with 75 cc. of water. After stirring thoroughly, 25 cc. alcohol are added and the solution allowed to stand for at least one hour. The lead sulphate is filtered off on a Gooch crucible, washed with water containing about 1% of sulphuric acid and 25% of alcohol and then with pure alcohol until free from acid. It is dried on the hot plate and weighed.

The **copper** is best determined electrolytically. The filtrate from the lead sulphate is heated on the hot plate until most of the alcohol is expelled. Two cc. concentrated nitric acid are added and the warm solution (about 60°) electrolyzed with a current of ½ to 1 ampere for about six hours. If a gauze electrode is used or one of the electrodes is rotated the time required is very much reduced.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic, antimony,* or unseparated *tin* which may be present. If more than traces are found, the metals must be separated and determined by the methods given in the preceding methods. When the amount of copper is large, as is generally the case, it is advisable to divide the solution into two portions for the electrolysis, as about 300 milligrams of copper is generally sufficient for a good determination. The solution may be divided by weighing it and then pouring out about half of it and again weighing or the solution may be diluted to a known volume as 250 or 500 cc. and a portion measured out. The copper may be determined in each portion and the filtrates combined for the zinc determination. For the duplicate zinc determination the copper may be precipitated as sulphide, which is filtered off, well washed, and discarded.

Iron. The filtrate from the copper is boiled to expel hydrogen sulphide and a little nitric acid added to oxidize the iron, which is precipitated with ammonia and weighed as oxide. If more than a small amount of iron is present, the pre-

cipitate must be redissolved and reprecipitated to separate it completely from the zinc.

Zinc. The filtrate from the iron is evaporated to small bulk and the zinc precipitated and weighed as pyrophosphate. The zinc may also be precipitated and weighed as sulphide.

Analysis of German Silver

Alloy of Copper, Zinc, and Nickel, with Small Amounts of Lead, Iron, and Tin

One gram of the alloy is weighed out and dissolved in nitric acid as directed in the preceding exercise. The *tin, lead,* and *copper* are determined as directed in the same exercise.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic, antimony, tin,* or unseparated *copper* which may be present. If more than traces are found, the metals must be separated and determined by the methods given under Analysis of Type Metal, page 660.

Zinc. The filtrate is boiled until the hydrogen sulphide is expelled and the solution concentrated to a small bulk and the acid nearly neutralized with caustic soda. Five to 10 grams of caustic soda are dissolved in about 50 cc. of water and the solution of zinc and nickel added slowly with constant stirring. The solution is diluted with an equal bulk of water and the precipitate filtered off and washed. The zinc in the filtrate is precipitated with hydrogen sulphide, filtered off, and washed free from alkali. The zinc sulphide is dried and detached from the paper as completely as possible.

The portion still adhering to the paper is dissolved in nitric acid and the solution evaporated to dryness in a porcelain crucible. The remainder of the precipitate is added and the whole ignited with sulphur in a stream of hydrogen. If the precipitate is small it need not be dried, but is immediately dissolved in nitric acid and after evaporation converted into sulphide. The sulphide is tested for alkali by digestion with hot water. If alkali is found, it must be completely extracted and the sulphide again weighed after ignition with sulphur in hydrogen. The precipitate is then dissolved in nitric acid and the solution evaporated to dryness. The zinc nitrate is dissolved in water and the silica filtered off, washed, ignited, and weighed. The zinc sulphide may also be dissolved in hydrochloric acid, the zinc precipitated as zinc ammonium phosphate and weighed as pyrophosphate.

Iron and Nickel. If iron is absent, the nickel hydroxide may be washed and after transferring the precipitate to a weighed porcelain crucible and burning the paper it may be reduced to metallic nickel by heating in a stream of hydrogen and weighed. If iron is present, the precipitate is dissolved in hydrochloric acid and the iron precipitated with ammonia. Unless a very small amount is present it must be redissolved and reprecipitated, and, after washing, is ignited and weighed as oxide. The nickel is then reprecipitated as hydroxide by means of an excess of caustic soda, reduced in a stream of hydrogen and weighed as the metal.

Analysis of Manganese-Phosphorus-Bronze

Alloy of Copper, Lead, Tin, Zinc, Manganese, Phosphorus (less than 1%), Traces of Iron

Solution. One gram of the alloy is weighed out and dissolved in nitric acid. Nearly all of the phosphorus remains with the stannic oxide as a phosphate. After fusing the impure precipitate and separating the impurities, and precipitating the tin as sulphide, the solution containing only the phosphorus as phosphoric acid is discarded, as this element is determined in a separate portion of the alloy.

Lead, Copper, and Zinc are determined as given under Analysis of Brass and Bronze, page 668. The phosphoric acid which did not remain with the stannic oxide will be present in the alkaline solution of the zinc. This element should therefore be precipitated and weighed as pyrophosphate.

Iron. In order to separate manganese and iron from zinc, bromine or hydrogen peroxide is added to the filtrate from the copper. The solution is boiled and excess of ammonium added to redissolve any zinc phosphate which may be precipitated. The precipitate consisting of ferric hydroxide and manganese dioxide is filtered off and washed. It is dissolved in a little hydrochloric acid and the paper well washed. The solution is boiled until the chlorine is completely expelled, then neutralized with ammonia, warmed, and the trace of iron filtered off immediately. Unless the precipitate is very small it is redissolved in hydrochloric acid and again precipitated with ammonia and quickly filtered off and washed. It is ignited and weighed as oxide.

Manganese. The combined filtrates from the iron contain all of the manganese unless the amount of iron present is considerable. The solution should be evaporated to dryness in a porcelain dish and the ammonium chloride volatilized by gently heating with the Bunsen burner. The residue is dissolved in a few cc. of water and a few drops of hydrochloric acid and the manganese precipitated and weighed as sulphide.

Volumetric Determination of Iron and Manganese. If considerable iron is present, the method of separation given is not applicable. In this case the simplest methods of determining the two metals are volumetric. The ammonium precipitate should be dissolved in sulphuric acid with the addition of a little hydrogen peroxide, the excess of which may be expelled by boiling. The solution must be made up to a definite volume and divided into two equal portions. For this purpose a 100-cc. flask should be used which has been calibrated with a 50-cc. pipette by emptying the pipette twice into the dry flask and making a mark on the stem. The solution of iron and manganese is evaporated to small bulk, transferred to the flask, made up to the mark and thoroughly mixed. Fifty cc. are withdrawn with the dry pipette. The solution adhering to the walls of the pipette is rinsed out with distilled water and added to the portion remaining in the flask. One of these portions is reduced with zinc and the iron titrated with standard permanganate. (See p. 219.) The other portion is shaken up with zinc oxide until the free acid is neutralized. One gram of zinc sulphate and a drop or two of dilute nitric acid are added and the solution diluted to several hundred cubic centimeters. The manganese is titrated with standard potassium permanganate according to Volhard. (See page 266.)

Phosphorus. For the determination of phosphorus a 5-gram portion of the alloy is taken, as the percentage of this element is usually small (seldom more than

0.2%). The material is placed in a 200-cc. beaker and 20 to 30 cc. concentrated nitric acid added. The beaker is covered with a watch-crystal and after the first violent action of the acid has ceased it is placed on the water bath and heated until the alloy is completely decomposed and the residue is pure white. All of the phosphoric acid will remain with the tin provided a sufficient amount of the latter is present in the alloy. From six to eight times as much tin as P_2O_5 must be present. Unless at least 5% of tin has been found, a preliminary test should be made by dissolving about a gram of the alloy in concentrated nitric acid, filtering, and testing the filtrate for phosphoric acid with molybdate mixture. If phosphoric acid is found in the filtrate, metallic tin must be added before dissolving the alloy in nitric acid. From ½ to 1 gram will usually be found sufficient.

The nitric acid solution of the alloy is diluted and the stannic oxide containing the phosphoric acid is filtered off and washed a few times. After drying, the precipitate is transferred to a porcelain crucible, the paper is burned, and the ash added. After adding three times its weight of potassium cyanide, cover the crucible and fuse for a few minutes at a red heat. The stannic oxide is reduced to metallic tin and the phosphoric acid forms potassium phosphate. After cooling, extract the fused mass with hot water, filter, and wash the paper with hot water.

Expel the hydrocyanic and cyanic acids by boiling with concentrated hydrochloric acid. *This operation must be conducted under a hood with good draught.* Evaporate to dryness to dehydrate the silicic acid which has been dissolved from the porcelain by the action of the potassium cyanide. Dissolve the dry residue in a little hydrochloric acid and pass hydrogen sulphide to precipitate a small amount of tin and copper which is present. Filter, wash the precipitate, and destroy the hydrogen sulphide in the filtrate by adding bromine water and boiling. If the volume of the solution exceeds 50 cc., concentrate by boiling. Cool and precipitate the phosphoric acid by adding about ½ gram of crystallized magnesium chloride or sulphate dissolved in a little water and then neutralizing the solution with filtered ammonia while stirring vigorously. Add a small excess of ammonia. Assure yourself that the phosphoric acid is all precipitated by adding a little magnesia mixture to the clear supernatant liquid. After standing several hours, filter, wash with dilute ammonia, ignite in a porcelain crucible, and weigh as magnesium pyrophosphate.

The precipitation of the metals present with hydrogen sulphide may be omitted and the separation effected by precipitating the phosphoric acid as molybdate. The dry residue should then be dissolved in nitric acid, and after filtering off the silica, the phosphoric acid is precipitated as directed in the chapter on Phosphorus.

METHODS FOR ANALYSIS OF COAL

FRANK E. HALE [1]

Such tremendous value attaches in boiler-room economy to the character of the fuel that the purchase of coal upon the results of laboratory analysis has grown in importance. Specifications have been drawn with such exact requirements that fairness to the coal contractor requires that only exact methods of analysis be employed.

SAMPLING

In order that the laboratory sample shall be representative of the delivery, great care must be taken, however; the personal element should be eliminated as far as possible. When possible, coal should be delivered by chutes and a shovelful taken at regular intervals throughout the delivery. If delivered in wagons a portion should be taken from each wagon load. Boat loads are best sampled while being loaded or unloaded. If a pile of coal must be sampled, portions should be taken from all sides, top and bottom. The gross sample should preferably be 200 pounds for deliveries up to 100 tons and one-tenth of 1% of the amount delivered for quantities over 100 tons. Larger sizes should be crushed to at least pea size (about $\frac{3}{4}$ in.) and preferably under. The gross sample should be thoroughly mixed with a shovel, piled up, and quartered. Opposite quarters should then be mixed, piled up, and quartered again and this continued until a sample of about 5 pounds is obtained.[2] This sample should then be forwarded to the laboratory in a sealed moisture-tight container. The most satisfactory container is one made of galvanized iron, to prevent rusting, cylindrical in shape with screw cap flush with the sides. A convenient size is 6 ins. in diameter by 8 ins. height. Such a can is readily cleaned and sealed. Sealing is conveniently made by pasting a strip of paper around the can over the joint, or by means of wax and an impression seal.

PREPARATION OF SAMPLE FOR ANALYSIS

The laboratory sample should first receive a number which should follow the sample through all phases of preparation in order to avoid confusion. The whole sample, when received at the laboratory, should be crushed to 4-mesh size or less. The Chipmunk Jaw Crusher is rapid and easily cleaned, as one jaw is removable. If too wet to crush, causing clogging of the crusher, the whole sample should be dried on the steam bath, the moisture so lost determined and added to the analytical moisture later determined on the pulverized sample. Shallow agateware pans large enough to take the complete sample are convenient and should set in large holes on the steam bath, so that the body of

[1] Director of Laboratories, Dept. Water Supply, Gas and Electricity, New York City.

[2] The U. S. Bureau of Mines uses a 3-pound sample and New York City a 7-pound sample.

the pan is exposed to the steam and drying is hastened. A few hours only is necessary. The U. S. Bureau of Mines dries in a special oven with a current of dried air at 30–35° C., but this occasions a delay of twelve to ninety-six hours. The crushed sample should be mixed and quartered, preferably by hand. This is best and most rapidly done in the old-fashioned way by raising alternately the corners of a large piece of oilcloth or rubber sheet. The pile may be quickly quartered by two V-shaped pieces of galvanized iron to cut and pull away opposite quarters. The remaining quarters should be again mixed and quartered in the same way and the process continued until a 100-gram representative

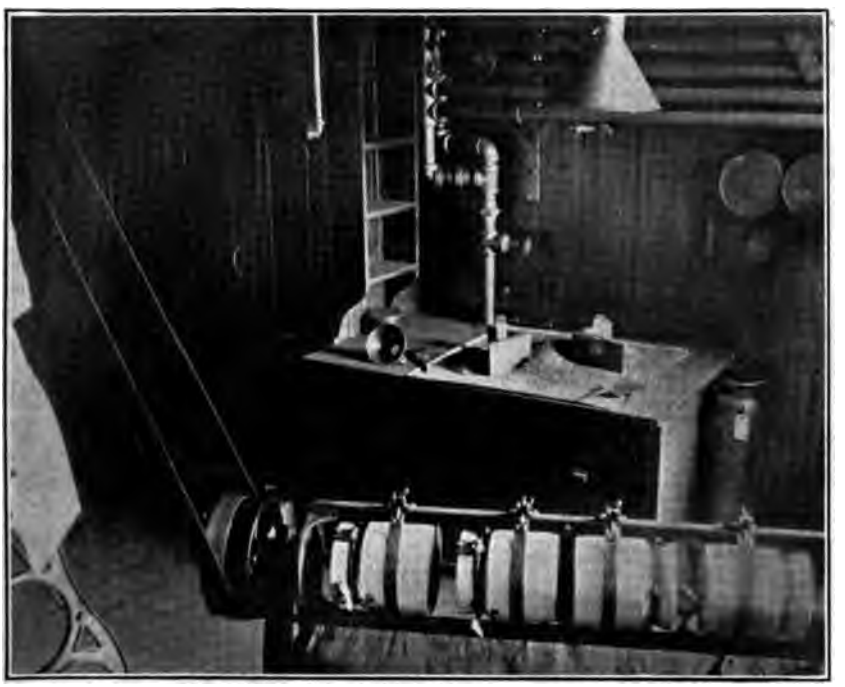


FIG. 103.—Illustrates Method of Quartering Coal, Ball Mill for Pulverizing, and Suction Ventilator.

portion is obtained. The discarded quarters should be returned to the can to be retained in case a second analysis is desired. Such check analysis should always be made upon a freshly quartered and pulverized sample of the remaining portions of the original gross laboratory sample.

The 100-gram sample should then be pulverized in an Abbé Ball Mill for three-quarters of an hour. The jar should be nearly full to produce the most rapid pulverization, that is, contain the full charge of pebbles, about 10 pounds for the 9-in. jar. The speed of revolution should be 60 per minute. Natural flint pebbles are least abraded and produce no appreciable effect upon the ash. The ball mill has two distinct advantages. It conserves the moisture

of the coal and it pulverizes so fine that the coal will usually all pass a 60-mesh screen and a large part the 100-mesh screen. This greater fineness prevents incomplete combustion of anthracite coal in the bomb determination to be described later. The pebbles and coal should then be dumped on a covered ash-sifter resting on the oilcloth or rubber sheet, shaken quickly and pebbles and sifter brushed clean. The sample should then be passed through the 60-mesh screen and brushed at once into a moisture-tight container. Any material retained on the 60-mesh screen, which occasionally happens, should be quickly pulverized in a small steel mortar. One-half pint, glass-covered lightning jars are convenient for this purpose.

As the dust in coal sampling is so fine as to penetrate through the clothing to the skin, it is wise to use an aspirator to protect the lungs and also use a suction ventilator to keep the air fresh and clean. The suction should connect with small hoods over the crusher and over the quartering table.

METHODS OF ANALYSIS

Moisture. Moisture may be accurately determined on a 10-gram sample heated for one hour at 105° C. Close checks will be obtained and weighing is rapid, as the weight need only be taken to the nearest milligram. Glass evaporating dishes of 2¾-in. diameter are convenient for this determination. The Beans electric thermo-regulator for gas has been found very satisfactory for oven regulation, as the oven may be heated rapidly and will quickly come to adjustment.

Most laboratories employ a 1-gram sample, however, and later use the residue for ash determination. The Bureau of Mines uses a special drying oven and a specially prepared sample for moisture. The 4-mesh sample is crushed in a roll or coffee-mill crusher to 20-mesh, and bottled quickly without sieving.

Ash. The ash represents the mineral matter in coal after ignition. No attempt is made in common practice to calculate the original form of the constituents. It is best determined upon a separate portion of coal, and preferably in silica crucibles, as the wear on platinum is considerable. Heating should be slow and careful at first, to avoid loss from volatile matter and to avoid the effect of coking. Later the contents should be stirred with a platinum wire to facilitate combustion, not neglecting to tap the wire free from ash. The silica crucibles should rest on silica or nichrome triangles. Some laboratories employ a muffle furnace and others an electric furnace.

The residue from moisture may be used for ash determination, but the residue from volatile combustible matter should not be so used, as there is danger of mechanical loss of ash in the rapid heating, and the accuracy of the ash-figure is far more important than the volatile combustible matter.

A 1-gram sample is used for the ash determination.

Volatile Combustible Matter. This determination is entirely empirical and should be performed under strictly standard conditions. The determination is made upon a 1-gram sample heated for seven minutes, timed by a stop-watch, in a platinum crucible of 25-30 cc. capacity, and with tight-fitting cover. The crucible and cover should be kept brightly polished. A special apparatus should be arranged. Construct a cylinder of asbestos or galvanized iron to protect flame and crucible. Connect an adjustable Méker burner (Scimatco type is preferable) with a U-tube to measure gas pressure. Arrange a platinum

wire from triangle to support the bottom of crucible always at same distance from the burner.

Calibrate the apparatus by adjusting the burner and pressure so that the crucible is entirely surrounded by the flame and the temperature is about 950° C. This may be determined by an optical or other pyrometer, but most conveniently by the fusing-point of potassium chromate. Note the gas pressure required and in the analyses set the gas at this pressure. In this way close checks may conveniently be obtained when the right conditions have been determined.

The loss in weight minus the moisture is the volatile combustible matter.

A 10–20-cc. crucible has recently been advocated to reduce the effect of oxidation by oxygen in the crucible. Several different schemes have been advocated in order to obtain uniform results. An electric furnace is used by some. Any method is empirical, as the determination does not represent any

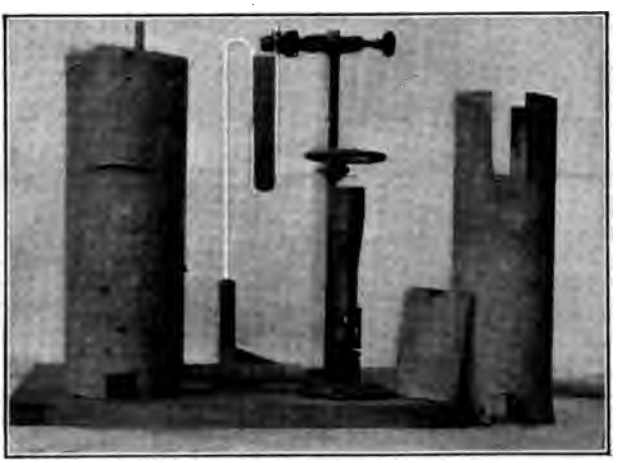


FIG. 104.—V. C. M. Apparatus

very definite constituent of the coal. Originally intended as a measure of coking ability the V.C.M. is now mainly a means of discriminating between different kinds of coal and as a means of keeping within the smoke ordinances.

Volatile Sulphur. The total sulphur in a coal is of little importance. If desired, it may be determined by the well-known Eschka method. The volatile sulphur is of great importance both in its bearing upon fusibility by indicating the presence of pyrites in the coal and in its relation to corrosion by the formation of sulphurous acid.

Volatile sulphur is determined in the bomb washings after a calorific determination. These washings are filtered if necessary and titrated for acidity for one of the corrections in the calorific calculation. The sulphur is then determined most rapidly and conveniently by a Jackson Candle Turbidimeter.

"The titrated solution is made up to 200 cc. The amount of acidity found is used as a guide in selecting the aliquot for the sulphur determination. In

TURBIDIMETRIC SULPHUR TABLE

For use with Jackson's candle turbidimeter

Sulphur and SO_2 contained in 100 cc. precipitated

Depth. Cm.	S. Mg.	SO_2. Mg.	Depth. Cm.	S. Mg.	SO_2. Mg.	Depth. Cm.	S. Mg.	SO_2. Mg.
1.0	20.0	50.0	5.0	3.66	9.15	9.0	2.30	5.75
1.1	18.0	45.0	5.1	3.60	9.00	9.1	2.28	5.70
1.2	16.5	41.3	5.2	3.54	8.85	9.2	2.26	5.65
1.3	15.0	37.5	5.3	3.49	8.73	9.3	2.25	5.63
1.4	13.5	33.8	5.4	3.43	8.58	9.4	2.23	5.58
1.5	12.5	31.3	5.5	3.38	8.45	9.5	2.21	5.53
1.6	11.2	28.0	5.6	3.33	8.33	9.6	2.19	5.48
1.7	10.0	25.0	5.7	3.28	8.20	9.7	2.18	5.45
1.8	9.5	23.8	5.8	3.24	8.10	9.8	2.16	5.40
1.9	9.0	22.5	5.9	3.20	8.00	9.9	2.15	5.38
2.0	8.5	21.3	6.0	3.15	7.88	10.0	2.13	5.33
2.1	8.0	20.0	6.1	3.11	7.78	10.1	2.11	5.28
2.2	7.6	19.0	6.2	3.07	7.68	10.2	2.10	5.25
2.3	7.3	18.3	6.3	3.03	7.58	10.3	2.09	5.23
2.4	7.0	17.5	6.4	2.99	7.48	10.4	2.07	5.18
2.5	6.7	16.8	6.5	2.95	7.38	10.5	2.06	5.15
2.6	6.5	16.3	6.6	2.92	7.30	10.6	2.04	5.10
2.7	6.3	15.8	6.7	2.88	7.20	10.7	2.03	5.08
2.8	6.1	15.3	6.8	2.85	7.13	10.8	2.02	5.05
2.9	5.9	14.8	6.9	2.82	7.05	10.9	2.01	5.03
3.0	5.7	14.3	7.0	2.79	6.98	11.0	2.00	5.00
3.1	5.5	13.8	7.1	2.76	6.90	11.1	1.98	4.95
3.2	5.4	13.5	7.2	2.73	6.83	11.2	1.97	4.93
3.3	5.2	13.0	7.3	2.70	6.75	11.3	1.95	4.88
3.4	5.1	12.8	7.4	2.67	6.68	11.4	1.94	4.85
3.5	5.0	12.5	7.5	2.64	6.60	11.5	1.93	4.83
3.6	4.85	12.25	7.6	2.61	6.53	11.6	1.92	4.80
3.7	4.75	12.00	7.7	2.59	6.48	11.7	1.91	4.78
3.8	4.63	11.75	7.8	2.56	6.40	11.8	1.90	4.75
3.9	4.52	11.50	7.9	2.54	6.35	11.9	1.89	4.73
4.0	4.43	11.25	8.0	2.51	6.28	12.0	1.88	4.70
4.1	4.33	11.00	8.1	2.49	6.23	12.1	1.87	4.68
4.2	4.24	10.75	8.2	2.47	6.18	12.2	1.86	4.65
4.3	4.16	10.50	8.3	2.44	6.10	12.3	1.85	4.63
4.4	4.08	10.25	8.4	2.42	6.05	12.4	1.84	4.60
4.5	4.00	10.00	8.5	2.40	6.00	12.5	1.83	4.58
4.6	3.93	9.83	8.6	2.38	5.95	12.6	1.82	4.55
4.7	3.86	9.65	8.7	2.36	5.90	12.7	1.81	4.53
4.8	3.79	9.48	8.8	2.34	5.85	12.8	1.80	4.50
4.9	3.72	9.30	8.9	2.32	5.80	12.9	1.79	4.48

TURBIDIMETRIC SULPHUR TABLE.—*Continued*

Depth. Cm.	S. Mg.	SO_2. Mg.	Depth. Cm.	S. Mg.	SO_2. Mg.	Depth. Cm.	S. Mg.	SO_2. Mg.
13.0	1.78	4.45	17.1	1.49	3.73	21.1	1.24	3.10
13.1	1.77	4.43	17.2	1.49	3.73	21.2	1.23	3.08
13.2	1.76	4.40	17.3	1.48	3.70	21.3	1.23	3.08
13.3	1.75	4.38	17.4	1.47	3.68	21.4	1.22	3.05
13.4	1.74	4.35	17.5	1.47	3.68	21.5	1.21	3.03
13.5	1.73	4.33	17.6	1.46	3.65	21.6	1.21	3.03
13.6	1.73	4.33	17.7	1.45	3.63	21.7	1.20	3.00
13.7	1.72	4.30	17.8	1.44	3.60	21.8	1.20	3.00
13.8	1.71	4.28	17.9	1.44	3.60	21.9	1.19	2.98
13.9	1.70	4.25	18.0	1.43	3.58	22.0	1.18	2.95
14.0	1.70	4.25	18.1	1.43	3.58	22.1	1.18	2.95
14.1	1.69	4.23	18.2	1.42	3.55	22.2	1.17	2.93
14.2	1.68	4.20	18.3	1.41	3.53	22.3	1.16	2.90
14.3	1.67	4.18	18.4	1.41	3.53	22.4	1.16	2.90
14.4	1.66	4.15	18.5	1.40	3.50	22.5	1.15	2.88
14.5	1.66	4.15	18.6	1.40	3.50	22.6	1.15	2.88
14.6	1.65	4.13	18.7	1.39	3.48	22.7	1.14	2.85
14.7	1.64	4.10	18.8	1.38	3.45	22.8	1.13	2.83
14.8	1.63	4.08	18.9	1.38	3.45	22.9	1.13	2.83
14.9	1.62	4.05	19.0	1.37	3.43	23.0	1.12	2.80
15.0	1.62	4.05	19.1	1.37	3.43	23.1	1.11	2.78
15.1	1.61	4.03	19.2	1.36	3.40	23.2	1.11	2.78
15.2	1.60	4.00	19.3	1.35	3.38	23.3	1.10	2.75
15.3	1.60	4.00	19.4	1.35	3.38	23.4	1.09	2.73
15.4	1.59	3.98	19.5	1.34	3.35	23.5	1.08	2.70
15.5	1.59	3.98	19.6	1.34	3.35	23.6	1.08	2.70
15.6	1.58	3.95	19.7	1.33	3.33	23.7	1.07	2.68
15.7	1.57	3.93	19.8	1.32	3.30	23.8	1.06	2.65
15.8	1.57	3.93	19.9	1.32	3.30	23.9	1.05	2.63
15.9	1.56	3.90	20.0	1.31	3.28	24.0	1.05	2.63
16.0	1.56	3.90	20.1	1.30	3.25	24.1	1.04	2.60
16.1	1.55	3.88	20.2	1.30	3.25	24.2	1.03	2.58
16.2	1.54	3.85	20.3	1.29	3.23	24.3	1.03	2.58
16.3	1.54	3.85	20.4	1.28	3.20	24.4	1.02	2.55
16.4	1.53	3.83	20.5	1.28	3.20	24.5	1.02	2.55
16.5	1.53	3.83	20.6	1.27	3.18	24.6	1.01	2.53
16.6	1.52	3.80	20.7	1.26	3.15	24.7	1.01	2.53
16.7	1.52	3.80	20.8	1.26	3.15	24.8	1.00	2.50
16.8	1.51	3.78	20.9	1.25	3.13	24.9	1.00	2.50
16.9	1.50	3.75	21.0	1.25	3.13	25.0	1.00	2.50
17.0	1.50	3.75						

the case of anthracite coals, the amount taken is one-fourth to one-half; in the case of soft coals from one-fourth to one-tenth of the whole."

"The aliquot of the solution to be tested is measured into the turbidimeter tube, diluted to near the 100-cc. mark, shaken, then acidified with 1 cc. of 1 : 1 hydrochloric acid, made up to the mark, and mixed well by shaking. A barium chloride tablet[1] weighing 1 gram and compressed without the use of a binder is then dropped in and the tube closed by means of a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity.

When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; but violent shaking should be avoided, since it would have a tendency to cause aggregation of the precipitate. The turbid liquid is then transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a moment after each addition until the liquid in the tube is quiet, and continuing thus until the image of the flame just disappears. The depth of the liquid in centimeters is noted. The mixture is then returned to the beaker, poured back and forth from beaker to tube two or three times, and read again as before.

"The precipitated solution is read at least twice, and the readings usually check exactly, unless they fall in the upper part of the tube, where they may differ by a centimeter without materially altering the results. In this case readings may be averaged. The amount of sulphur corresponding to the depth of liquid in the tube is found in the table, and multiplied by the proper factor, depending on the aliquot of the original solution taken.

"All dilutions must be made before precipitation, for otherwise the results will not be concordant for different dilutions." The average time required is ten minutes or less. The method carried out as described is accurate to about 0.05% sulphur.

Fixed Carbon. Fixed carbon is found by adding the moisture, ash, and volatile matter together, and subtracting from 100%.

Calorific Value. Heat value is expressed as "small calorie (cal.)," the amount of heat required to raise the temperature of 1 gram of water 1° C., "large calorie (Cal.)," the amount of heat required to raise the temperature of 1 kilogram of water 1° C., and "British thermal unit (B.t.u.)," the amount of heat required to raise the temperature of 1 pound of water 1° F., at or near 39.1° F. Small calories per gram of coal multiplied by 1.8 equal B.t.u. per pound of coal.

It is preferable to express results as B.t.u. per pound of dry coal, instead of coal as received, since comparison between different samples of coal and the results of different analysts and laboratories are facilitated. The other determinations except moisture are also better expressed on the dry basis.

[1] These tablets are prepared on order by the Fraser Tablet Co., of Brooklyn, N. Y., Formula No. 188,663.

On standing for some time, some of the tablets become coated with a thin layer of effloresced salt. This should be removed by gently rubbing between the fingers before using the tablet. It is not advisable to keep the tablets in a moist atmosphere to prevent this efflorescence, as they become extremely hard and difficult to dissolve.

As a check upon accuracy of work and to catch errors, results of B.t.u. should also be calculated to B.t.u. per pound of combustible, that is, divide the B.t.u. dry basis by (100% minus the per cent of ash). For the same run of coal, this value changes but little, usually within 200 B.t.u.

The calorific determination should be made by means of a bomb calorimeter. The platinum-lined Atwater type is very convenient and requires but little repair.

One gram of the 60-mesh sample of coal prepared for analysis is weighed into a nickel capsule (28 mm. top width, 23 mm. bottom width, and 12 mm.

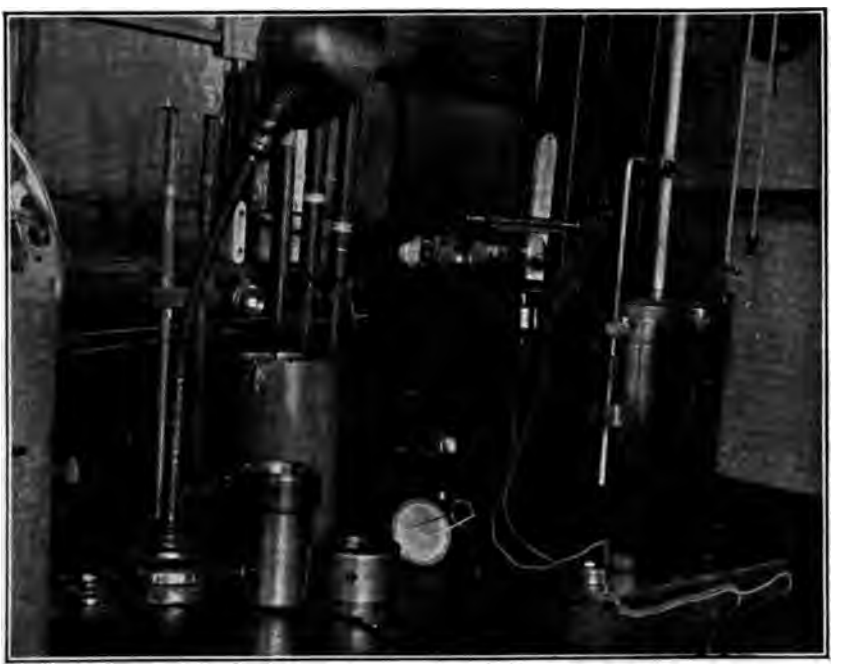


FIG. 105.—Atwater Bomb and Calorimeter with Accessories, in Special Room.

depth) in the bottom of which has been placed an ignited disc of asbestos paper. The latter prevents incomplete combustion of anthracite coal by preventing chilling of the coal after combustion starts. In weighing large numbers of samples a piece of tared platinum foil is convenient and the coal transferred with a camel's-hair brush into the nickel capsule. The capsule is supported on a platinum ring suspended by a platinum wire from the head of the bomb. A piece of iron fuse wire, No. 34 B. & S. gauge, and weighing 10 milligrams, is attached at one end to the wire supporting the tray and at the other end to another platinum wire extending downward from the head, but insulated from it. Attachment of the fuse wire is made by winding around the platinum wires several times. The center of the fuse wire should dip into the coal slightly. A convenient method of obtaining pieces of fuse wire of uniform weight is to wind around a flat piece of board or cardboard and cut the loops.

The shell of the bomb is rinsed with water and sufficient moisture, one-half cc., is thus left to take up the acids formed by combustion. The head is next joined gas tight to the shell of the bomb by the collar. Lead gaskets render these joints tight. Oxygen gas is slowly introduced, so as not to blow the coal out of the pan, until about 21 atmospheres pressure is recorded in the bomb. The needle valve is then closed just tight enough to prevent leakage. the valve on oxygen tank closed and the bomb disconnected. Twenty atmospheres pressure should remain in the bomb for the combustion, an amount

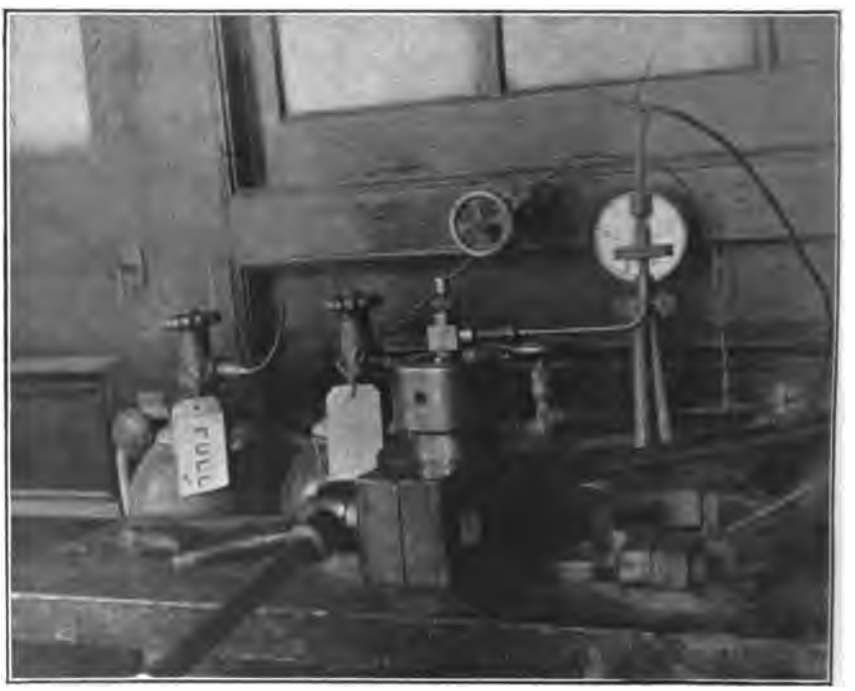


FIG. 106.—Illustrates Method of Connecting Two Oxygen Cylinders for Filling Bomb when Pressure in One is below Twenty Atmospheres.

sufficient for complete combustion of the coal and an amount containing sufficient nitrogen together with the nitrogen in the air trapped in the bomb to cause the sulphur to burn to sulphuric acid completely, unless the sulphur is unusually high.

The bucket is filled with enough distilled water, about 3° C. below the room temperature, to make the water equivalent of the calorimeter some round number, for example, 2000 grams with the Atwater, 2900 grams with the Mahler. The water is best weighed on a balance, capable of delicacy with such heavy weights, and the amount of water should be sufficient to cover the bomb. The bomb is placed in its support and placed in the water in the bucket. The latter is set in the calorimeter, the stirrer added so as not to touch bomb or bucket,

covers applied and thermometer placed in the water and adjusted so that it can be read during the combustion. The thermometers should be special and standardized by the Bureau of Standards. The Fuess type of Beckmann is excellent.

Connect the poles of six dry cells to the stem and insulated post of the bomb. Connection should be made with a button for firing the coal. It is also convenient to have a small electric lamp connected with the button to indicate that the batteries are in condition, before a run is started.

The calorific determination should be made in a room protected from sudden changes of temperature and from draughts. If a current of air strikes the thermometer during a determination, the results will be untrustworthy. Mechanical stirring is preferable and should be at a moderate rate. The stirrer is started and after a couple of minutes or so, when conditions have become uniform, the thermometer is read by means of a telescope and readings taken every one-half minute for six readings. Interpolate to the 0.001° C. A clock striking every half minute is convenient. After the sixth reading, fire the coal by pressing the button connected with the batteries and take approximate readings of the thermometer every half minute, reading to the 0.001° C. as soon as the rise is slow enough to do so. After the maximum temperature has been reached, take six more readings at half-minute intervals.

Remove the bomb from the bucket and allow the gas to escape slowly. Disconnect the head and rinse out the bomb thoroughly. Titrate the washings with N/10 sodium carbonate, using methyl orange as indicator. Determine the sulphur, after titration, with the turbidimeter as under Volatile Sulphur.

Calculation of B.T.U. The table on page 682 is an example of an actual determination, showing corrections as applied.

Corrections must be applied to the thermometer in accordance with the certificate furnished for each thermometer by the Bureau of Standards, including the correction for temperature of setting of Beckmann thermometers and emergent stem correction for others.

The thermometer should also be fitted with a vibrator to overcome meniscus error. This is conveniently done by arranging a small electric vibrator so that the hammer hits the rubber-covered metal clamp supporting the thermometer. The vibrator should, of course, be connected to a push-button and dry batteries.

Correction must also be made for changes of temperature due to radiation. A simple formula which yields results within 0.002° C. as compared with the more elaborate formulæ is the following:

$$\frac{x(a+b)}{2}+yb = \text{radiation correction.}$$

a = average preliminary period change per half minute;

b = average final period change per half minute;

x = number of half-minute intervals of combustion period during which the rise of temperature (expressed to the nearest 0.01°) was greater than 10% of the total rise. This is readily seen by inspection;

y = remaining number of half-minute intervals of combustion period.

The algebraic signs must be observed in the formula.

The end of the combustion period is taken as the first reading after the maximum temperature. The reason for this rests in the fact that the real maximum rarely occurs at a half-minute interval reading, as shown by a drop during the first period after the maximum temperature read, of less than the

NO. 1 BUCKWHEAT COAL

Thermometer used (T_5), zero set at 20.4° C.

Room Temperature 22.5° C. Atwater bomb.

Acid found equal 7.2 cc. N/10 $Na_2CO_3 \times 1.45$ cal.	= 10.4 calories
Volatile sulphur (aliquot ½) 8.6 cm. = .0048 gram × 13 cal.	= 6.2 calories
Iron wire (10 milligrams)	= 16.0 calories
	32.6 calories

Thermometer readings, Half minute intervals	
Preliminary period	0.979
	0.980
	0.981
	0.983
	0.984
	0.986
Average rise in temperature: $\frac{.007}{5} = .0014$	
Combustion period	1.600
	3.270
	4.050
	4.225
	4.267
	4.278
	4.279
	4.278
Final period	4.273
	4.270
	4.268
	4.264
	4.260
Average fall in temperature: $\frac{.018}{5} = .0036$	

Corrected temperature, end of combustion period	4.277
Corrected temperature, end of preliminary period	0.986
Apparent rise in temperature corrected for thermometer calibration	3.291
Thermometer correction for setting and room temperature	+0.022
Apparent rise in temperature, corrected for thermometer setting	3.313
Radiation correction: $3\left(\frac{(-.0014)+(+.0036)}{2}\right)+5(+.0036)$	+0.021
Corrected rise in temperature	3.334
Water equivalent (grams)	2000
Calories (2000 × 3.334)	6668.0
Correction for acidity, sulphur trioxide and iron	32.6
Actual calories, coal as received	6635.4
Calories (dry basis) 6635.4 ÷ .9522 (100% − moisture)	6968.5
B.t.u. per lb. of coal (dry basis) (6968.5 × 1.8)	12,543
B.t.u. per lb. of combustible (dry basis) 12543 ÷ .842(100% − ash)	14,897

B.T.U.	12,543
V.C.M.	7.7 %
Ash	15.8
Vol. sulphur	0.48
Moisture	4.78

average final change. Correcting for an extra combustion interval counteracts this error.

The nitrogen in the coal and in the air of the bomb forms nitric acid. This does not occur when coal is burned in the furnace, hence the bomb determination is too high by the amount of heat thus produced. The calorific value of nitrogen burning to nitric acid is 230 calories per gram of nitric acid. Each

ubic centimeter of N/10 sodium carbonate used in the titration represents .45 calories.

Furthermore, sulphur in the furnace burns to the dioxide and in the bomb to the trioxide. This excess heat in the bomb must be corrected for as well as the fact that all of the above acidity is not nitric, but is partly sulphuric acid. This correction is conveniently made by adding to the acidity correction (made as if it were all nitric acid) 13 calories for each 0.01 gram of sulphur. This represents the excess which the oxidation correction is over its expression as the formation of nitric acid as obtained from the titration.

The correction for the iron fuse wire is 16 calories for each 10 milligrams.

All other corrections are met by standardization under conditions similar to those under which the calorimeter is to be used. Such errors arise from loss of heat by evaporation of water while stirring (probably covered by the radiation correction), gain in heat due to combustible gases in the oxygen, changes in specific heat of water at various temperatures, changes in the gases present after combustion, and changes of pressure of the gases in the bomb. The last three errors are too small to take into account. The oxygen error has disappeared since the introduction of the purer gas manufactured by the Linde Air Products Company.

Inspection of the bomb contents should always be made to insure that there are no sooty deposits or coal thrown from the capsule. Some coals require to be compressed into pellets to prevent the above.

The procedure outlined above, using half-minute intervals, saves considerable time (nearly one-half) over the usual procedure and produces very accurate results.

Standardization of the Calorimeter. While there are several ways of determining the water equivalent of the calorimeter, that is, the heat capacity of the apparatus expressed as though it were all water, only one method should be used by commercial laboratories, and that is to burn in the calorimeter a known weight of pure substance, the calorific value of which has been determined by the Bureau of Standards, Washington, D. C. Of those furnished, benzoic acid is preferable, as it readily ignites and burns completely. If cane sugar should be used, a few milligrams of benzoic acid are necessary to assist ignition and correction must be made for its heating value. Cane sugar does not always burn completely.

Procure standardized benzoic acid from the Bureau of Standards. Compress into pellets by means of pellet press sufficient benzoic acid to produce approximately as many calories as are given by the coal, that is, about 7000 calories. One gram of benzoic acid produces 6320 calories. Determine in the calorimeter the temperature rise produced by the benzoic acid with the precautions used in a regular coal analysis, correcting for thermometer and radiation errors. Multiply the grams of benzoic acid taken by 6320 calories, add the calories produced by formation of nitric acid as obtained from the titration and add the calories produced by the iron fuse wire. Divide this sum by the corrected rise in temperature. The quotient is the water-equivalent of the calorimeter. The amount of water added to the bucket is then changed so as to make the total calorimeter equivalent a round number, such as 2000 for the Atwater or 2900 for the Mahler. The amount of water should be sufficient to entirely immerse the bomb and avoid spattering by the stirrer. Then restandardize with the new quantity of water. The conditions of combustion should be as closely as possible like those prevailing during regular coal analysis.

DETERMINATION OF FUSIBILITY OF COAL ASH

This determination has become of increasing importance in recent yea especially in relation to mechanical stokers and gas manufacture. The co position of the ash, not its amount, is the determining factor. Alumina them ost refractory constituent and its fusing-point, 2000° C., is lowered prop

FIG. 107.—Hoskins Electric Furnace, Optical Pyrometer in Position. Also (X) Metho of Supporting Cone in Graphite Block.

tionately to the amounts of silica, alkalies, and iron present. In many co the amounts of all but the latter do not lower the fusing-point sufficiently cause trouble, that is, below 1400° C. The amount of iron becomes then supreme importance, as the last straw that breaks the camel's back. This popularly shown in the classification of coals as red ash and white ash. T

condition of the iron is of great importance also, as in the ferric condition it has but slight effect, but in ferrous condition it lowers the fusion-point greatly. The influence of sulphur upon fusing-point probably depends upon the accompanying presence of iron as pyrites. In the coal bed in the presence of burning carbon the ferric oxide may be reduced to ferrous oxide or not, according to the care of the fire and the amount of oxygen supplied. This explains discrepancies occurring between the facts of clinkering of the coal on the grates and the fusing-point as determined in a laboratory furnace. The fusing-point varies in different types of furnaces for the same reasons. It seems safest to choose such furnaces in laboratory tests as give reducing atmospheres and hence lower fusing-point, indicating the possible danger.

A convenient furnace, for high temperatures especially, is the Hoskins Electric Furnace. The heat is generated by passing a heavy alternating current of low voltage through a series of carbon plates. Temperature is regulated by compression of these plates. This furnace uses a 60-cycle alternating current, 220 volts, about 40 amperes. The current is transformed by an air-cooled transformer to a current of 10 volts. The maximum temperature produced by the furnace is about 2000° C.

The coal is burned to ash at as low a temperature as possible in clay dishes. The ash is moistened with water and moulded into the shape of a Seger cone ($\frac{1}{2}$ in. by $2\frac{1}{2}$ ins.) by pressing into a mould conveniently made of lead. A piece of thin paper, moistened, is laid in the mould to facilitate removal of the cone. Some coals may require 10% dextrin paste as a binder, but it is usually unnecessary. The use of smaller cones has recently been advocated. The cones may be set in triangular holes in a Dixon graphite block and placed in the furnace so that the cone is horizontal. This position gives as concordant results as the vertical position, if not closer. The fusing-point is taken when the cone droops into a vertical position. The temperature must not rise too rapidly when near the fusing-point, about 5° C. per minute. The temperature is conveniently read by a fixed-focus total-radiation pyrometer or an optical pyrometer of the Wanner type. Reducing atmospheres preclude the use of metallic couples at high temperatures.

NOTE. The methods in this chapter are based upon those in use at the Mt. Prospect Laboratory, of the Department of Water Supply, Gas and Electricity, New York City. The method for fusibility was obtained originally from the Laboratory of the Consolidated Gas Company, New York City.

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GAS ANALYSIS

AUGUSTUS H. GILL[1]

SAMPLING

The process consists in the insertion of a suitable tube into the flue or duct, and the withdrawal of the gas sought, by some sort of pump.

Tubes. The tube employed varies with the nature of the gas and its temperature. Ordinarily, a combustion tube a meter long of 16–17 mm. outside diameter, which has been drawn down to 7 mm. at one end, to facilitate the attachment of rubber tubing, is used. These soften at about 500° C. For higher temperatures we have a choice of quartz, porcelain tubes of about the same dimensions, or water-cooled metal tubes. Uncooled metal tubes cannot be employed above 250° without danger of reduction of the oxides of the metals composing the tube, by the carbonic oxide contained in the gases.[2] If porcelain

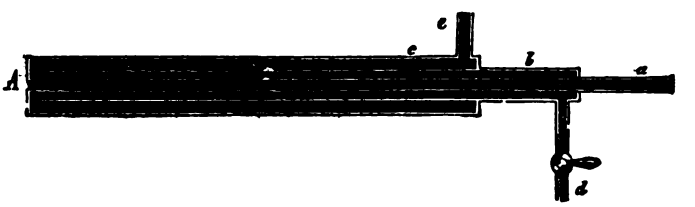

FIG. 108.

tubes be used, they should be glazed within and without, to prevent the transfusion through them of the lighter gases like methane and hydrogen: they, as well as glass tubes, should be warmed before insertion into a hot flue. The construction of the water-cooled tubes will be evident from Fig. 108.

For cooling the gas, the tube should not be inserted to its full length. Rolls of wire gauze can be inserted near the cool, drawn-out end of the tube: these will serve for the removal of soot and dust. The removal of dust may be further effected by the use of plugs of asbestos or glass wool.

The place from which the gas is collected should be so chosen as to give a representative sample, and all openings except those intended for the inlet of air, stopped up. In a circular duct or chimney the average velocity of the gases is usually at a point one-third the distance from the wall to the center. In case of a boiler, the setting should be carefully inspected, all cracks filled with mortar, and the clean out doors made tight. The fact that bricks themselves are porous must not be lost sight of, and new settings should be sized and given a coat of whitewash. If possible the tube should be inserted below the damper to avoid

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[2] Fischer, "Technologie der Brennstoffe," 1880, p. 221, cites an instance in which CO_2 was changed from 1.5 in the mixture, to 26% by the passage through an iron tube heated to dull redness.

leakage from that source. A second hole should be made for the introduction an oil tube for the thermometer. The joints around these tubes should be ma tight with mortar, plaster of Paris, or in the case of a temporary connectio putty or wet cotton waste. Care should be taken not to insert the tube so clo to the source of heat as to withdraw the gases in a dissociated or partially decor posed condition. For sampling the gases from different zones of a blast furnac water-cooled tubes are made which can be screwed together to produce th desired length.

Pumps. Where a sufficient head of water (15 or 20 lbs. is enough for ou purpose) is available, the Richards jet pump, Fig. 109, may be used. This can b easily constructed in glass as shown in Fig. 110 and the glass jets drawn down to suit the water pressure. It may be noted that the pump may be operated with steam equally as well as with water.

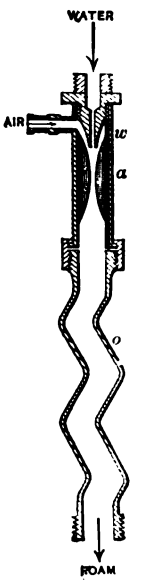


FIG. 109.

FIG. 110.

In case a head of water be not accessible, pumps employing a fall of water — the Bunsen pump, Fig. 111, may be used. This consists essentially of a quarter-inch tee, one branch of which is connected with the water supply, another with the vessel to be evacuated, while the third is connected with 10[1] or 15 ft. of quarter-inch pipe, preferably lead. The water in this acts as a moving piston and draws the gas in after it.

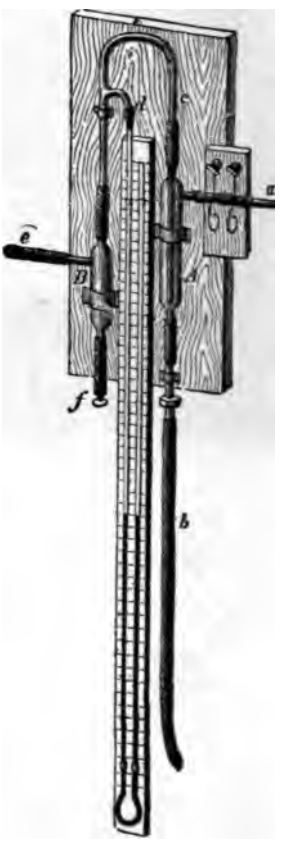


FIG. 111.

Where none of these is available, some type of a power-driven pump, or an ordinary rubber syringe bulb may be employed. Instead of these, two aspirator bottles—of gallon or two-gallon size—will furnish the necessary suction. These are made by passing two glass tubes bent at right angles through each rubber stopper fitting the bottles: one branch of one elbow stops just under the stopper, while a branch of the other goes to the bottom of the bottle. The tubes carrying the long branches are connected by a 3- or 4-foot piece of quarter-inch rubber tubing provided with a screw pinch-cock. Upon setting one bottle higher than the other and blowing into its shorter tube, water siphons through the longer into the lower bottle, producing suction in the upper. This is sometimes used for taking a continuous sample extending

[1] For the highest vacuum over 32 ft.—the height of the water barometer.

over several hours. Strong brine is a suitable solution for the bottles, since it possesses the advantage over water in absorbing less carbon dioxide.

Containers for Samples. These are of glass, preferably of the shape shown in Fig. 112. Being pear shaped, the vessel is completely emptied, leaving no liquid to exercise a solvent action on the gas. The tubing shown in the figure is of lead, which can be safely used for chimney gases after it becomes attacked by them. Its obvious advantage is found in the fact that it bends rather than breaks. Glass bottles—parts of the aspirator just described—may be used; the rubber connection should be thick, carefully wired on and provided with screw pinchcocks. The long tube should carry a short piece of rubber tubing within the bottle reaching to its side; by tipping it the water can be more completely run out through this tube. The use of metal containers in general is not recommended, as those of zinc or galvanized iron are attacked by carbon dioxide; where the gases do not act upon the metals they may of course be advantageously employed. To ensure tightness, the rubber stoppers used should be held in by screws which fit into a brass plate on top of the stopper and into wire loops about the neck of the bottle. This compresses the stopper about the tubes and into the bottle neck, making a thoroughly tight joint. Or the brass plate may be replaced by a piece of sole leather and wire passed over this after the manner of wiring down the bottles containing carbonated waters.

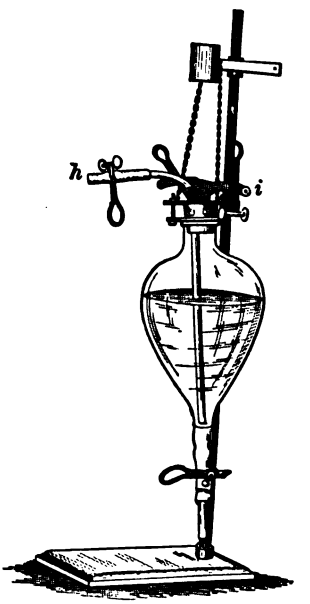


FIG. 112.

The use of rubber bags is not to be recommended, as they absorb certain gases and are oxidized by others: the most satisfactory containers are glass tubes provided with drawn-out ends which can be sealed in the lamp flame.

In connecting up the sampling tube, container and pump, the use of rubber tubing is to be avoided as much as possible for the reason just given.

MEASUREMENT OF GAS IN LARGE QUANTITIES. METERS

Several types of instruments are available for this purpose.

The wet meter, The dry meter } Measure total gas passed—not for acid gases.

The Pitot tube or Davis anemometer
The Rotameter or Thorp gauge
The Capometer
The Thomas electric meter
The orifice meter
The anemometer
} All these measure velocity simply

} For all gases particularly acid

The first two meters show all the gas passing through the system while the others simply measure the rate of flow: with these the size of the pipe must be

known. Of all these instruments, the wet meter and Thomas meter are probably the most accurate. They, however, like some of the others, cannot be used with corrosive gases, being constructed of metal; hence the Pitot tube, rotameter and capometer are the ones to be employed in chemical works.

The **wet meter** consists of a cylindrical drum divided into four spiral compartments, suspended in a bath of water, surrounded by a tight casing: the pressure of the gas causes the drum to rotate, emptying a drumful of gas into the casing and pipes. It must be set level, the water level carefully adjusted to the mark on the glass gauge, with its top open, as well as the inlet and outlet pipes of the meter. The higher the water level the faster the meter. The **dry meter** consists of a pair of metal bellows, with sides of leather soaked in oil, on either side of a diaphragm, and connected with slide valves so that a bellowsful of gas is alternately emptied into the upper part of the meter and piping. The vibrations of the bellows produced by the gas pressure are transmitted to clockwork and indexes. It is to be noted that the indexes apparently read one-tenth of the actual volume passed: the index must make a complete circuit to register the amount stamped on the dial. A small index and dial are usually present for testing the meter, and a tolerance of 2% is allowed by law. This testing is done by meter-provers, carefully calibrated gas holders kept at constant temperature and the rate determined at different speeds. The meter-provers are, in their turn, calibrated by a cubic foot, standardized at the Bureau of Standards. It should be noted that all this calibration is corrected, not to standard conditions (0° C. and 760 mm.), but to the cubic foot as fixed by law—gas saturated with moisture at 60° F. and 30 inches.

The Pitot Tube. Fig. 113. This consists of two glass-tubes, D, of about $\frac{1}{4}$ inch internal diameter, inserted in the gas stream: one is bent at right angles and is set so that it receives the impact of the gas movement; the other merely registers the pressure of the gas in the pipe. The point of insertion of these tubes in the chimney or duct should be in a long straight run of pipe, so as to be as free from eddies as possible. Davis[1] says that authorities differ as to whether the tubes should be a third or one-sixth of the diameter from the circumference to show the mean speed: he states further that each flue or chimney is a separate problem and as a result of hundreds of measurements there seems to be "no settled proportionate distance corresponding to the mean velocity."

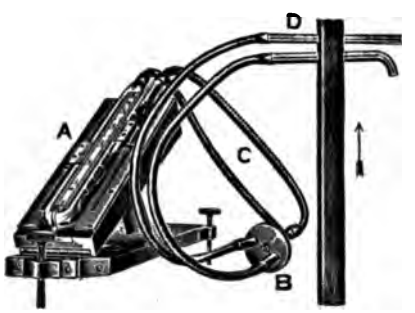


FIG. 113.

The glass tubes are connected by rubber tubing, C, through a reverser, E, with a U-tube A, which is either set vertically, inclined 30°, or one in ten—this carries a vernier reading to hundredths of an inch so that readings to thousandths are feasible. The U-tube is filled with solutions of different specific gravity, although ether of 0.74 sp.gr. is the one commonly employed. The difference between the arms of the U-tube represents the difference between the kinetic and static pressures of the gas in the flue or chimney.

[1] "Handbook of Chemical Engineering," 1, 197, also for the tables for its use.

The formulæ for calculating the velocity are $V=\sqrt{p\times 28.55}$ where V = velocity in feet per second, p the anemometer reading, or twice the height of the ether column, the gas being at a temperature of 15.5° C. (60° F.) and 30 inches barometric pressure. As this, however, rarely occurs, the formula is

$$V_0=\sqrt{p\frac{459+t^\circ}{519}}\times 28.55$$

giving the speed for the high temperature (°F.).

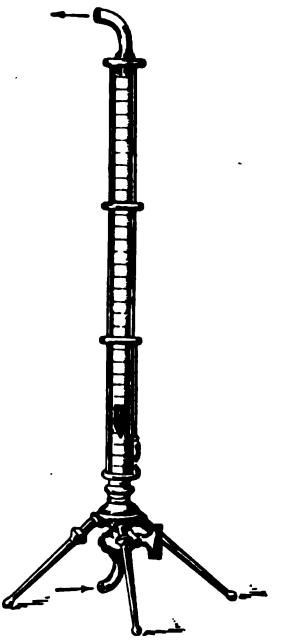


FIG. 114.

The Rotameter,[1] Fig. 114. This is a German instrument depending upon the height to which a float is carried in a glass tube by the velocity of the stream of gas. A modification of it was used by some of the gas-lighting companies under the name of the Thorp gauge.

It consists of a graduated glass tube fixed upon a tripod and provided with a plumb line so that it can be set vertically: gas passes in at the lower end, raises the clay or talc float to a certain height and passes out at the top. The height to which the float is raised is noted on the graduations of the tube. The formula for its use is

$$V_1=V\sqrt{\frac{M}{M'}}.$$

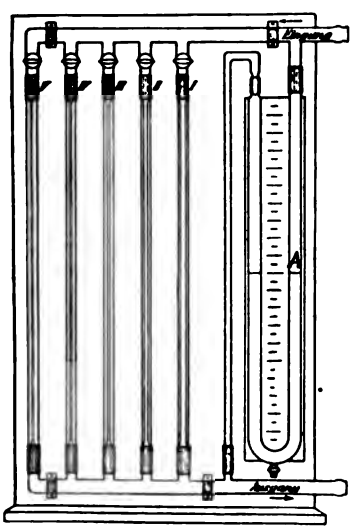


FIG. 115.

V = volume gas as shown by reading of instrument, M its specific gravity = 1.0.

V = volume desired, M_1 = sp.gr. of gas.

It is made in all capacities from 0.2 cu.ft., per hour up.

The Capometer.[2] Fig. 115. This consists of a series of capillary tubes of different sizes through which the gas is made to pass and the pressure thus produced noted in the U-tube A. Each capillary is calibrated and curves of gas flow are made corresponding to different pressures in the U-tube and various capillaries. An instrument made with capillaries 1–4 mm. in diameter has a capacity of 0.004 to 70 cu.ft. per hour.

The Thomas Electric Gas Meter.[3] This depends upon the principle that if the specific heat of the gas be known, and an amount of energy be put into it, by means of a coil, sufficient to keep a certain difference

[1] Anon., Ch. Abs., 5, 1695, 1911.
[2] J. Gasbeleuchtung, 55, 557, 1912.
[3] Thomas, J. Frank. Inst., 172, 411.

of temperature between two thermometers, one before and one after the coil, this energy is a direct measure of the volume of gas flowing. Two electrical thermometers are placed in the stream of gas with a heating coil between them: 2° difference of temperature is automatically maintained between the thermometers and the energy to preserve this difference of temperature (.0127 watt hour per standard unit of gas) is read off on the meter as cubic feet of gas. It is independent of temperature or pressure changes in the gas, and is used up to gas pressures of 180 lbs. per square inch. This is used in a Western gas works measuring 200,000 ft. of gas per hour.

The Orifice Meter. In this the same principle is used as in measuring water, by determining the diminution in pressure as registered on delicate gauges before and after the gas has passed through a standard orifice. It is largely used for measuring natural gas.

The anemometer is used ordinarily for measuring currents of air leaving or entering a room, analogous to its employment in meteorology.

MEASUREMENT OF GAS IN SMALL QUANTITIES. GAS BURETTES

Here may be mentioned the Hempel gas burette, made for accurate work with a compensation tube; the bulbed Orsat or Bunte burette; the separatory funnel and graduate.

The Hempel Gas Burette, Fig. 122, consists of a 100-cc. burette graduated in fifths of a cubic centimeter, provided with a short capillary at the top and closed with a rubber connector and pinch-cock, and a wider tube at the bottom, over which the $\frac{1}{8}$-in. rubber tube is drawn, which connects it with the leveling tube of similar size and length to the burette. Like all volumetric instruments, it should be carefully calibrated. It is manipulated by filling the leveling tube completely with water, opening the pinch-cock on the top of the burette and filling it with water. The gas to be analyzed is sucked in and measured as with the Orsat apparatus, p. 697.

For accurate work the burette is enclosed in a water jacket, connected with a compensating tube also contained in water jacket, and provided with a manometer so that changes in temperature or pressure may be neutralized. Mercury, instead of water, is the confining liquid. Instead of a straight tube, Bleier [1] used one consisting of a string of bulbs of about 10-cc. capacity: by means of a side connection with a graduated 10-cc. burette, volumes of 10-cc. multiples and fractions can be measured. The **Orsat,** Fig. 120, and **Elliott apparatus,** Fig. 121, use bulbed burettes to shorten them, connected with leveling bottles.

Separatory Funnel and Graduate, Fig. 130. From the water which has flowed out, the quantity of gas can be determined. See p. 721.

[1] Berichte, **31**, 1, 238.

ABSORPTION APPARATUS, TUBES, AND PIPETTES

These are quite varied according to the purpose for which they are intended. A very efficient form is the Friedrichs Spiral Gas Washing bottle, Fig. 116; here the gas has to pass through a long spiral path. Dennis[1] recommends this for the absorption of sulphur dioxide. The gas is run through a solution until a color change takes place. Were the reagent to be washed out and titrated it would not seem so well adapted on account of the difficulty of thoroughly washing it.

The Varrentrapp and Will bulbs, Fig. 117, the use of which is evident from the figure, are used for the absorption of ammonia in illuminating gas. The Wolff

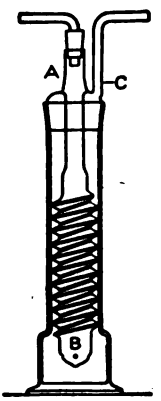


FIG. 116.

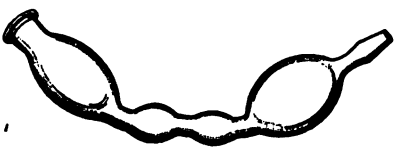


FIG. 117.

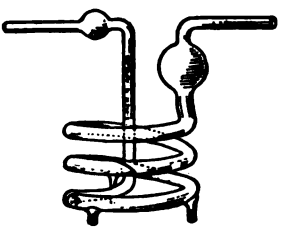


FIG. 119.

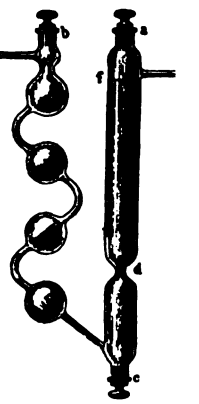


FIG. 118.

absorption tube, Fig. 118, the empty arm of which is filled with beads or broken glass is used for the absorption of carbon monoxide by blood. The bulbed tube, provided with a small jet, is generally used for containing standard solutions of acid, alkali, or potassium permanganate or, in general, a solution which is to be titrated after absorption. Where the presence of a gas as, for example, water vapor, is to be determined by the increase of weight of the reagent used, Winkler's spiral, Fig. 119[2], may be employed.

Pipettes—Particularly for the Orsat Apparatus. These are ordinarily filled with glass tubes, but various modifications have been proposed: these are the bubbling type of Hankus, the spiral bubbling variety of Nowicki-Heinz and a combination of the Friedrichs wash bottle proposed by Dennis. All these suffer from the very serious disadvantage of a glass three-way stopcock at the top, which it is practically impossible to prevent from sticking, unless the apparatus be used by one person and that one exceptionally careful and painstaking. Dennis[3] has shown that one variety is no more rapid than the original and some of the others but little more so. When it is further considered that they cost four times as much,[4] their use would seem of doubtful expediency.

[1] "Gas Analysis," p. 274, 1913.
[2] Called "Winkler's Bulbs" in the apparatus catalogs.
[3] Ibid., p. 83.
[4] Ten dollars.

It is interesting to note further that Anderson [1] has shown that with the modified potassium pyrogallate which he uses, the original Orsat slightly modified, to allow the precipitate to settle, is the best.

EXAMINATION OF THE GASES

The qualitative examination of a gaseous mixture is rarely resorted to in technical work: a sufficiently close idea of the gases present can be obtained by a consideration of the reactions involved in the various operations. It is, however, not safe to rely upon this in matters of importance, as conditions may change: for example if the gases be dry or dilute, hydrogen sulphide and sulphurous anhydride can exist together. Similarly in sewage gases, all the gas absorbed by cuprous chloride is probably not carbon monoxide. The means of identifying the different gases will be found under each gas.

Detection and Determination of the Various Gases

Clemens Winkler divided the gases into seven groups according to their behavior with various solvents. These were contained in suitable absorption tubes or vessels and the gases passed through them. His scheme was as follows:

Gases absorbed by

I. H_2SO_4 1.7 sp.gr.; NH_3, (N_2O_3), N_2O_4.
II. KOH 1.3 sp.gr.; Cl_2, HCl, $(CN)_2$, HCN, SO_2, H_2S, SiF_4, CO_2.
III. $AgNO_3$; PH_3, AsH_3, SbH_3.
IV. Pyro; O_2, (O_3).
V. CuCl; CO.
VI. Acid $FeSO_4$ 1:2; NO.
VII. Unabsorbed; H_2, CH_4, C_2H_2, C_2H_4, N_2O, N_2, COS, and the noble gases.

The following tables give the specific gravity referred to air, the solubility in water at 20°, the qualitative tests and quantitative methods of determination of these gases: additional means will be found mentioned under the several gases themselves.

GROUP I

Gases Absorbed by H_2SO_4 1.7 *sp.gr.*

Name	Ammonia.	Nitrous anhydride.	Nitrogen tetroxide.
Gravity, air = 1	0.589		1.590
Qualitative Tests	Fumes w. HCl on a rod. Nessler's reagent.	Acts like a mixture of NO and NO_2.	Absorb in KOH, test for nitrites.
Quantitative Det'n	Absorption in standard acid. Or $3NaBrO+2NH_3=N_2+3NaBr+3H_2O$. Or absorption in water and Nesslerization. pp. 291, 537.		Absorption in N/10 $KMnO_4$. $2KMnO_4+10NO_2+3H_2SO_4+2H_2O=10HNO_3+K_2SO_4+2MnSO_4$. Or in standard alkali.
Solubility 20° C., 1 cc. water absorbs cc.	678		Forms $HNO_3.HNO_2$

[1] J. Ind. and Eng. Chem., 8, 131–3, 1916.

GROUP II

Gases Absorbed by KOH 1.3 *sp.gr.*

Name	Chlorine.	Hydrochloric acid.	Cyanogen.
Gravity, air = 1	2.449	1.259	1.799
Qualitative Test	KI starch paper.	Fumes w. NH_3.	Pass through mixture of $FeSO_4$ 1 : 10 + KOH, 1 : 3. and ppt. as Prussian blue w. ferric alum and H_2SO_4.[1]
Quantitative Det'n	$2KI + Cl_2 = 2KCl + I_2$. Or absorption w. KOH.	Absorption in standard alkali or silver nitrate.	
Solubility 20° C., 1 cc. water absorbs cc.	2.15	442	4.5

Hydrocyanic acid	Sulphur dioxide.	Hydrogen sulphide.	Silicon fluoride.	Carbon dioxide.
0.936	2.213	1.177	3.60	1.520
Absorption in KOH and $FeSO_4$ and $FeCl_2$ = Prussian blue. Absorption w. KOH or acid $AgNO_3$.[2]	Fuchsine paper bleached or KIO_3 starch paper. $SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$.	$PbAc_2$ paper, absorption by I solution. $H_2S + 2I = 2HI + S$.	None $3SiF_4 + 4H_2O = SiO_4H_4 + 2H_2SiF_6$.	BaO_2H_2 on black rod. Absorption w. KOH or BaO_2H_2 and titration.
Very sol.	36.4	2.67	Decomposed.	0.892

GROUP III

Gases Absorbed by $AgNO_3$.

Name	Hydrogen phosphide, Phosphine.	Hydrogen arsenide, arsine.	Hydrogen antimonide, stibine.
Gravity, air = 1	1.175	2.696	4.330
Qualitative Test	Neutral H_2O Solution $KI + HgI_2$ = cryst. orange yel. ppt. $PHgI_3$.[3]	Blk. ppt. of $AsAg_3$ w. $AgNO_3$.	Blk. ppt. of $SbAg_3$ w. $AgNO_3$.
Quantitative Det'n	Pass through Br water and ppt. H_3PO_4 as usual.	Absorb w. NaClO cont. 3% Cl.[4]	Decompose w. tartaric acid and det. Sb.
Solubility 20° C., 1 cc. water absorbs cc.	0.02	about 5	Slight.

[1] Nauss, J. Gasbeleuchtung, **43**, 969, 1900.
[2] Rhodes, J. Ind. and Eng. Ch., **4**, 652, 1912.
[3] Lemoult, Compt. rend, **139**, 478, 1904.
[4] Reckleben, Z. ang. Ch., **19**, 275, 1906.

	Group IV		Group V	Group VI
	Absorbed by potassium pyrogallate		*Absorbed by cuprous chloride*	*Absorbed by $FeSO_4$ 1 : 2 acidulated w. H_2SO_4*
Name	Oxygen.	Ozone.	Carbon monoxide.	Nitric oxide.
Gravity, air = 1	1.105	1.62	0.967	1.038
Qualitative Test	Darkening of light brown "pyro."	$MnCl_2$ paper; KI Starch paper, N_2O_4 and H_2O_2 being removed by $KMnO_4$.	Absorb in blood, and examine w. spectroscope.	Oxidize, absorb in KOH and test for nitrites.
Quantitative Det'n	By "Pyro." CuCl in absence of CO.		Absorption w. CuCl.	Absorb in $FeSO_4$ 1 : 2 acidulated w. H_2SO_4 or with $KMnO_4$ as N_2O_4.
Solubility 20° C., 1 cc. water absorbs cc.	0.028	0.6 at 0°	0.023	0.267

	Group VII *Unabsorbed*			
Name	Hydrogen.	Methane.	thylene (ethene).	Acetylene (ethine).
Gravity, air = 1	.0696	0.554	0.968	0.899
Qualitative Test	None.	None.		Red ppt. w. am. CuCl (explosive!).
Quantitative Det'n	By combustion or explosion w. O_2.	By combustion or explosion w. O_2.	Absorption w. Br water or $H_2S_2O_7$	As C_2H_2, which see.
Solubility 20° C., 1 cc. water absorbs cc.	0.0182	0.035	0.15	1.03

Nitrous oxide.	Carbon oxysulphide.	Nitrogen.	The noble gases.
1.523	2.074	0.970	Helium, Neon, Argon, Krypton, Xenon.
None. By explosion with H_2 or combustion w. CuO.	None. Alcoholic KOH 1 : 3 in 66% alcohol by weight.	None. By absorption or combustion of all other gases and measuring the residue which also contains the noble gases.	
0.670	0.3	0.014	

NOTES. GROUP I: NaBrO is made by saturating a 10% solution of caustic soda with bromine.

GROUP II: Chlorine can be removed from hydrochloric acid by passing the gases over finely powdered antimony: hydrochloric acid can be removed from chlorine by means of manganese dioxide or zinc oxide.

The following reactions will serve to discriminate between HCN and $(CN)_2$:

$(CN)_2+2H_2O+(HCl)=2CO(NH_2)_2+(HCl)$ oxamide.

$HCN+2H_2O+(HCl)=HCOOH+NH_3+(HCl)$ formic acid.

Cyanogen is not absorbed by acid silver nitrate solution, from which it can be separated by drawing air through it: hydrocyanic acid is precipitated under these conditions.

GROUP IV: Ozone can be determined by Wurster's [1] method, consisting in passing the gas over paper moistened with *fresh* para phenylene diamine [2] and comparing the depth of color produced with a standard paper. In large quantities it can be determined according to Treadwell and Anneler [3] by passing through standard neutral potassium iodide and titration of the liberated iodine with N/10 sodium thiosulphate.

Analysis of Gaseous Mixtures

The analysis of a gaseous mixture is effected by absorbing the various constituents and observing the diminution in volume: in case the gas be unabsorbable, as for example methane (CH_4), it is burned and the carbon dioxide and water determined.

(*a*) *Analysis of mixtures for carbon dioxide, oxygen and carbon monoxide* (*e.g. chimney gases, producer and blast furnace gas*) can be done with any of the apparatus to be described. The Orsat, or Elliott are the forms usually employed.

(*b*) *Analysis of mixtures as in* (*a*) and also containing *combustible gases* as *hydrogen and methane*, e.g., illuminating gas.

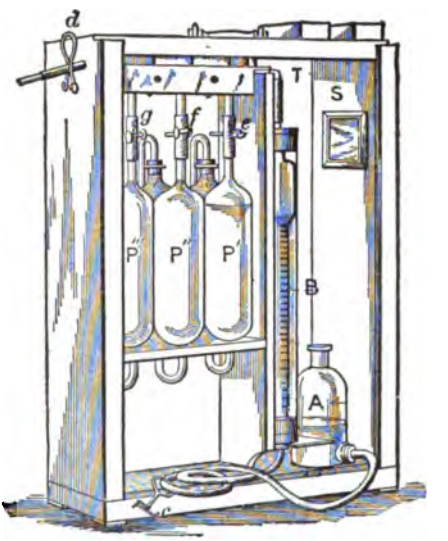


FIG. 120.

The Orsat Apparatus. Description. The apparatus, Fig. 120, is enclosed in a case to permit of transportation from place to place; furthermore, the measuring-tube is jacketed with water to prevent changes of temperature affecting the gas-volume. The apparatus consists essentially of the leveling-bottle *A*, the burette *B*, the pipettes *P'*, *P''*, *P'''*, and the connecting tube *T*. Pipette *P'* is filled with potassium (or sodium) hydroxide solution (see Reagents) so that when it is drawn up into the front arm about half an inch in depth is left in the rear arm. Pipettes *P''* and *P'''* are similarly filled with potassium (or sodium) pyrogallate and cuprous chloride solutions respectively. These reagents require to be pro-

[1] Berichte, **20**, 921 (1888).
[2] Obtainable from Schuchardt, Görlitz.
[3] Treadwell-Hall, "Quantitative Analysis."

tected from the oxygen of the air by collapsible rubber bags. As the oxygen in the air over the reagent is absorbed, a diminution in pressure takes place rendering it difficult to bring the reagent to the point on the stem: the obvious remedy is to remove the bag temporarily and adjust the reagent. When the apparatus is is first set up, one or two blank analyses should be made, to saturate the water and reagents with the gases. For example the potassium hydroxide absorbs carbon dioxide, it also absorbs about 3 cc. of oxygen, 2 cc. of carbon monoxide and 1.5 cc. of nitrogen, by virtue of the 100 cc. of water which it contains. A change of temperature of 1° makes a change of 0.36% of the volume of the gas: a change of pressure of 1 mm. produces 0.13% change in the volume.

Manipulation. The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette and the rubber connector. This is effected by opening wide the pinchcock upon the connector, the bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 cc., so that an error of half an inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening *d* and raising the leveling-bottle. The apparatus is now ready to receive a sample of gas (or air for practice). In case a flue-gas is to be analyzed *d* is connected with *i*, Fig. 112, *A* lowered and about 102 cc. of the gas forced over by opening *h*; or *d* may be connected with a T-joint in the gas-stream; the burette after filling is allowed to drain one minute by the sand-glass, *c* snapped upon its rubber tube, and the bottle *A* raised to the top of the apparatus. By gradually opening *c* the water is allowed to run into the burette until the lower meniscus stands upon the 100 or 0 mark (according to the graduation of the apparatus). The gas taken is thus compressed into the space occupied by 100 cc., and by opening *d* the excess escapes. Open *c* and *bring the level of the water in the bottle to the same level as the water in the burette* and take the reading, which should be 100 cc. Special attention is called to this method of reading: if the bottle be raised, the gas is compressed; if lowered, it is expanded.

Determination of Carbon Dioxide. The gas to be analyzed is invariably passed first into pipette *P'*, containing potassium hydroxide for the absorption of carbon dioxide, by opening *e* and raising *A*. The gas displaces the reagent in the front part of the pipette, laying bare the tubes contained in it, which being covered with the reagent present a large absorptive surface to the gas; the reagent moves into the rear arm of the pipette, displacing the air over it into the flexible rubber bag which prevents its diffusion into the air. The gas is forced in and out of the pipette by raising and lowering *A*, the reagent finally brought approximately to its initial point on the stem of the pipette, the burette allowed to drain one minute, and the reading taken. The difference between this and the initial reading represents the cubic centimeters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed a second time into *P'* and the reading taken as before; these readings should agree within 0.1%.

Determination of Oxygen. The residue from the absorption of carbon dioxide is passed into the second pipette, *P''*, containing an alkaline solution of potassium pyrogallate, until no further absorption will take place. The difference between the reading obtained and that after the absorption of carbon dioxide, represents the number of cubic centimeters of oxygen present.

Determination of Carbon Monoxide. The residue from the absorption of oxygen is passed into the third pipette, P''', containing cuprous chloride, until no further absorption takes place; that is, in this case until readings agreeing exactly (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen, represents the number of cubic centimeters of carbonic oxide present.

Determination of Hydrocarbons. The residue left after all absorptions have been made may consist, in addition to nitrogen, the principal constituent, of hydrocarbons and hydrogen.

Accuracy. The apparatus gives results accurate to 0.2 of 1%, hence figures obtained by division to 0.01 should not be reported.

Time Required. About twenty minutes are required for an analysis; two may be made in twenty-five minutes, using two apparatus.

NOTES. The method of adjusting the reagents is the only one which has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinchcock *c* upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 cc. of gas is exactly analogous to filling a measure heaping full of grain and striking off the excess with a straightedge; it saves arithmetical work, as cubic centimeters read off represent per cent directly.

It often happens when *e* is opened, *c* being closed, that the reagent P' drops, due not to a leak, as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in P'' and P''' absorbing oxygen with great avidity, and hence if freely exposed to the air would soon become useless.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage present is so small, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given; if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon dioxide; similarly if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but also oxygen as well.

The use of pinchcocks and rubber tubes, original with the author, although recommended by Naef, is considered by Fischer to be inaccurate. The experience of the author, however, does not support this assertion, as they have been found to be fully as accurate as glass stopcocks, and very much less troublesome and expensive.

In case any potassium hydroxide or pyrogallate be sucked over into the tube *T* or water in *A*, the analysis is not spoiled, but may be proceeded with by connecting on water at *d*, opening this cock, and allowing the water to wash the tubes out thoroughly. The addition of a little hydrochloric acid to the water in the bottle *A* will neutralize the hydroxide or pyrogallate, and the washing may be postponed until convenient.

After each analysis the number of cubic centimeters of oxygen and carbonic oxide should be set down upon the ground-glass slip provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity (see Reagents) of each reagent, the condition of the apparatus is known at any time, and the reagent can be renewed in season to prevent incorrect analyses.

Elliott Apparatus. Description. The apparatus Fig. 121 consists of a burette holding 100 cc. graduated in tenths of a cubic centimeter and bulbed like the Bunte apparatus—the bulb holding about 30 cc.; it is connected with a leveling-bottle similar to the Orsat apparatus. The top of the burette ends in a capillary stopcock, the stem of which is ground square to admit of close connection with the "laboratory vessel," an ungraduated tube similar to the burette, except of 125 cc. capacity. The top of this "vessel" is also closed with a capillary stopcock, carrying by a ground-glass joint, or better a rubber stopper, a thistle-tube *F*, for the introduction of the reagents. The lower end of this "vessel" is closed by a rubber stopper carrying a three-way cock *o*, and connected with a leveling bottle *D*. The burette and vessel are held upon a block of wood—supported by a ring stand—by fine copper wire tightened by violin keys.

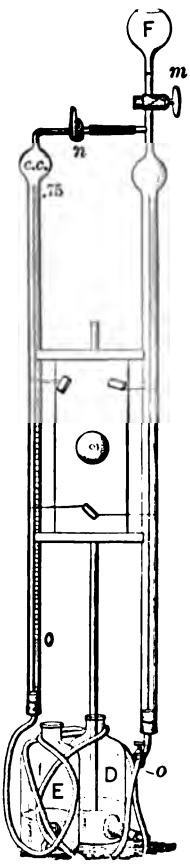


FIG. 121.

Manipulation. The ground-glass joints are lubricated with stopcock grease, p. 726. The leveling-bottles are filled with water, the stopcocks opened, and the bottles raised until the water flows through the stopcocks *m* and *n*. *m* is connected with the source whence the gas to be analyzed is to be taken, *n* is closed, *D* lowered and rather more than 100 cc. drawn in, and *m* closed. *n* is opened, *D* raised and *E* lowered, nearly 100 cc. of gas introduced, and *n* closed; by opening *m* and raising *D* the remainder of the gas is allowed to escape, the tubes being filled with water and *m* closed. *n* is opened and the water brought to the reference mark; the burette is allowed to drain one minute, the level of the water in *E* is brought to the same level as in the burette, and the reading taken.

Determination of Carbon Dioxide. By raising *E*, opening *n*, and lowering *D*, the gas is passed over into the laboratory vessel; *F* is filled within half an inch of the top with potassium hydroxide, *o* closed, *m* opened, and the reagent allowed slowly to trickle in. A No. 3 evaporating dish is placed under *o*, and this turned to allow the liquid in the laboratory vessel to run into the dish. At first this is mainly water, and may be thrown away; later it becomes diluted reagent and may be returned to the thistle-tube. When the depth of the reagent in the thistle-tube has lowered to half an inch, it should be refilled either with fresh or the diluted reagent and allowed to run in until the absorption is judged to be complete, and the gas passed back into the burette for measurement. To this end close *o* and then *m*, raise *E*, open *n*, and force some pure water into the laboratory vessel, thus rinsing out the capillary tube. Now raise *D* and lower *E*, shutting *n* when the liquid has arrived at the reference-mark. The burette is allowed to drain a minute, the level of the water in the bottle *E* brought to the same level as the water in the burette, and the reading taken.

Determination of Oxygen. The manipulation is the same as in the preceding determination, potassium pyrogallate being substituted for potassium hydrate; the apparatus requiring no washing out.

Determination of Carbonic Oxide. The laboratory vessel, thistle-tube, and bottle if necessary, are washed free from potassium pyrogallate and the absorption made with acid cuprous chloride similarly to the determination of carbon dioxide. The white precipitate of cuprous chloride may be dissolved by hydrochloric acid.

Accuracy and Time Required. The apparatus is as accurate for absorptions as that of Orsat; it is stated to be much more rapid—a claim which the writer cannot substantiate. It is not as portable, is more fragile, and more troublesome to manipulate, and as the burette is not jacketed, it is liable to be affected by changes of temperature.

NOTES. In case at any time it is desired to stop the influx of reagent, *o* should be closed first and then *m*; the reason being that the absorption may be so rapid as to suck air in through *o*, *m* being closed.

The stopcock should be so adjusted as to cause the reagent to spread itself as completely as possible over the sides of the burette.

By the addition of an explosion tube it is used for the analysis of illuminating gas,[1] bromine being used to absorb the "illuminants," Winkler[2] states that this absorption is incomplete; later work by Treadwell and Stokes, and also Korbuly,[3] has shown that bromine water, by a purely physical solution, does absorb the "illuminants" completely; Hempel[4] states that explosions of hydrocarbons made over water are inaccurate, so that the apparatus can be depended upon to give results upon methane and hydrogen only within about 2%. It is, however, very rapid, a complete analysis of illuminating gas can be made with it in fifty-five minutes.

Hempel's Apparatus. Description. The apparatus, Figs. 122 and 123, is very similar in principle to that of Orsat; the burette is longer, admitting of the reading of small quantities of gas, and the pipettes are separate and mounted in brass clamps on iron stands. *P* shows a "simple" pipette[5] provided with a rubber bag; this form, after twenty-five years of use, can be said satisfactorily to take the place of the cumbersome "compound" pipette.

The pipette for fuming sulphuric acid[6] is shown at *F*, and differs from the ordinary in that vertical tubes after the manner of those in the Orsat pipettes replace the usual glass beads. This prevents the trapping of any gas by the filling, which was so common with the beads and glass wool. *E* represents the large explosion pipette,[7] of about 250-cc. capacity, with walls half an inch thick; the explosion wires enter at the top and bottom to prevent short-circuiting; mercury is the confining liquid. The small explosion pipette holds about 110 cc. and is of glass, the same thickness as the simple pipettes. Water is here used as the confining liquid, and also usually in the burette.

An induction coil capable of giving a half-inch spark, with six dry cells, four "simple" pipettes and a mercury burette, complete the outfit.

The burette should be carefully calibrated and the corrections may very well be etched upon it opposite the 10-cc. divisions.

In working with the apparatus the pipettes are placed upon the adjustable stand *S* and connection made with the doubly bent capillary tube.

Manipulation. To acquire facility with the use of the apparatus before proceeding to the analysis of illuminating gas, it is well to make the following

[1] Mackintosh, Am. Chem. Jour., 9, 294.
[2] Zeit. f. Anal. Chem., 28, 286.
[3] Treadwell-Hall's "Quantitative Analysis," p. 569.
[4] "Gasanalytische Methoden," p. 102.
[5] Gill, Am. Chem. J., 14, 231, 1892.
[6] Ibid., J. Am. Chem. Soc., 18, 67, 1896.
[7] Gill, J. Am. Chem. Soc., 17, 771, 1895.

determinations, obtaining "check-readings" in every case: I. Oxygen in air, by (1) absorption with phosphorus; (2) absorption with potassium (or sodium) pyrogallate;[1] (3) by explosion with hydrogen.

I. DETERMINATION OF OXYGEN IN AIR

(1) By Phosphorus. 100 cc. of air are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus filling the capillary with water; the free end of the capillary is inserted into the

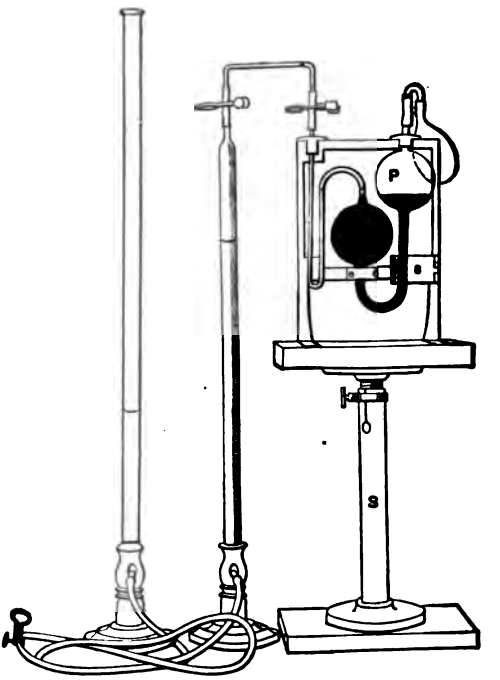


FIG. 122.

pipette connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcock on the burette and pipette are now opened, the air forced over into the phosphorus, and the pinchcock on the pipette closed; action immediately

[1] The writer finds after an experience of more than twenty-five years in the laboratory with hundreds of students, that sodium pyrogallate can be used with practically the same results as the potassium compound. The absorption is complete, as shown by subsequent treatment with cuprous chloride.

ensues, shown by the white fumes; after allowing it to stand fifteen minutes the residue is drawn back into the burette, the latter allowed to drain and the reading taken. The absorption goes on best at 20° C., not at all below 15° C.; it is very much retarded by small amounts of ethane and ammonia. It cannot be used to absorb commercial oxygen. No cognizance need be taken of the fog of oxides of phosphorus.

(2) By Pyrogallate of Potassium. 100 cc. of air[1] are measured out as before, the carbon dioxide absorbed with potassium hydrate and the oxygen with potassium pyrogallate, as with the Orsat apparatus; before setting aside the pyrogallate pipette, the number of cubic centimeters of oxygen absorbed should be noted upon the slate *s* on the stand. This must never be omitted with any pipette save pos-

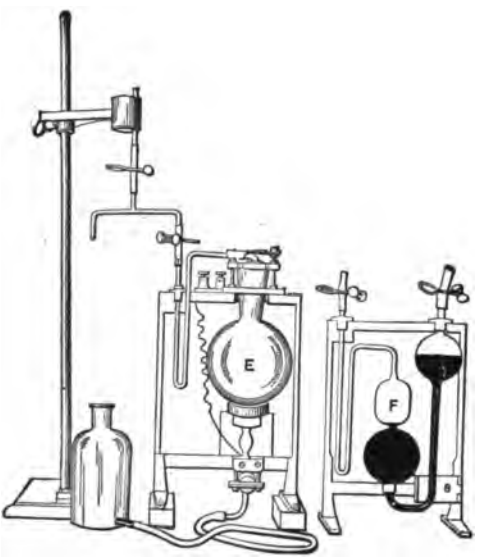


FIG. 123.

sibly that for potassium hydroxide, as failure to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity—four to five liters of carbon dioxide—of the reagent.

(3) By Explosion with Hydrogen. Forty-three cc. of air and 57 cc. of hydrogen are measured out, passed into the small explosion pipette, the capillary of the pipette filled with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases, otherwise some nitrogen will burn and high results will be obtained;[2] that is, $(H+O) : (N+H) :: 1 : 6$.

[1] See Anderson's work, J. Ind. and Chem., **7**, 587, 1915.

[2] This is shown in the work of Gill and Hunt, J. Am. Chem. Soc., **17**, 987, 1895.

II. ANALYSIS OF ILLUMINATING GAS

One hundred cc. of gas are measured from the bottle containing the sample into the burette.

Determination of Carbon Dioxide. The burette is connected with the pipette containing potassium hydroxide and the gas passed into it with shaking until no further diminution in volume takes place.

Illuminants, C_nH_{2n}, C_nH_{2n-6} Series.—The rubber connectors are carefully dried out with filter-paper, a dry capillary used, and the gas passed into the pipette containing fuming sulphuric acid and allowed to stand, with occasional passes to and fro, for forty-five minutes. On account of the extremely corrosive nature of the absorbent it is not advisable to shake the pipette, as in case of breakage a serious accident might occur. For water gas this is sufficient, although in case of doubt or with richer gases check readings to 0.2 cc. should be obtained. It is then passed into potassium hydroxide, as in the previous determination, to remove any sulphurous acid which may have been formed and any sulphuric anhydride vapor, these having a higher vapor tension than water. The difference between this last reading and that after the absorption of the carbon dioxide represents the volume of "illuminants" or "heavy hydrocarbons" present.

As has already been stated, page 701, saturated bromine water may replace the fuming sulphuric acid. Fuming nitric acid is not recommended, as it is liable to oxidize carbonic oxide.

Oxygen. This is absorbed, as in the analysis of air, by potassium or sodium pyrogallate.

Carbonic Oxide. The gas is now passed into ammoniacal cuprous chloride, until the reading is constant to 0.2 cc.; it is then passed into a second pipette, which is fresh, and absorption continued until constant readings are obtained. The second pipette should not have absorbed more than 10 cc. of CO.

Gautier and Clausmann[1] have shown that some carbonic oxide escapes solution in cuprous chloride, so that for very accurate work it may be necessary to pass the gas through a U-tube containing iodic anhydride heated to 70° C.

This is done by interposing this tube between the burette and a simple pipette filled with potassium hydrate. The reaction is $5CO+I_2O_5=5CO_2+2I$. The diminution in volume represents directly the volume of carbonic oxide present.

The volume of air contained in the tube should be corrected for as follows: One end of the tube is plugged tightly and the other end connected with the gas burette partly filled with air. A bath of water at 9° C. is placed around the U-tube and the reading of the air in the gas burette recorded when constant; the bath is now heated to 100° and the burette reading again recorded when constant. The increase in reading represents one-third the volume of the U-tube, $273 : 273+(100-9) :: 3 : 4$.

Methane and Hydrogen. (*a*) *Hinman's Method.*[2] The gas left from the absorption of carbonic oxide is passed into the large explosion pipette. About half the requisite quantity of oxygen (40 cc.) necessary to burn the gas is now added, mercury introduced through the T in the connector sufficient to seal the capillary of the explosion pipette, all rubber connectors carefully wired, the pinch-cocks closed, and the pipette cautiously shaken. A screen of heavy glass or fine wire gauze is interposed between the operator and the apparatus, the explosion

[1] Bull. Soc. Chem., **35**, 513; Abstr. Analyst, **31**, 349, 1906.
[2] Gill and Hunt, J. Am. Chem. Soc., **17**, 987, 1895.

wires are connected with the induction coil, a spark passed between them and the pinchcocks opened, sucking in the remainder of the oxygen. The capillary is again sealed with mercury, the stopcock opened and closed, to bring the contents of the pipette to atmospheric pressure, and the explosion repeated as before, and the stopcock opened.

It may be found expedient to increase the inflammability of the mixture, to introduce 5 cc. of "detonating gas," the hydrolytic mixture of hydrogen and oxygen. The gas in the pipette containing carbon dioxide, oxygen, and nitrogen is transferred to the mercury burette and accurately measured. The carbon dioxide resulting from the combustion of the marsh gas is determined by absorption in potassium hydroxide; to show the presence of an excess of oxygen, the amount remaining is determined by absorption with potassium pyrogallate.

The calculation is given on page 706. For very accurate work a second analysis should be made, making successive explosions, using the percentages of methane and hydrogen just found as a basis upon which to calculate the quantity of oxygen to be added each time. The explosive mixture should be so proportioned that the ratio of combustible gas (i.e., CH_4, H and O) is to the gases which do not burn (i.e., N and the excess of CH_4 and H) as 100 is to about 50 (from 26 to 64);[1] otherwise the heat developed is so great as to produce oxides of nitrogen, which, being absorbed in the potassium hydroxide, would affect the determination of both the methane and the hydrogen. The oxygen should preferably be pure, although commercial oxygen, the purity of which is known, can be used; the oxygen content of the latter should be tested from time to time, especially with different samples.

(*b*) *Hempel's Method.*[2] From 12 to 15 cc. of the gas are measured off into the burette (e.g., 13.2 cc.) and the residue is passed into the cuprous chloride pipette for safe keeping. That in the burette is now passed into the small explosion pipette; a volume of air more than sufficient to burn the gas, usually about 85 cc., is accurately measured and also passed into the explosion pipette, and in so doing water from the burette is allowed partially to fill the capillary of the pipette and act as a seal. The rubber connectors upon the capillaries of the burette and pipette are carefully wired on, both pinchcocks shut, and the stopcock closed. The pipette is cautiously shaken, the screen interposed, the explosion wires connected with the induction coil, a spark passed between them, and the stopcock immediately opened. The gas in the pipette, containing carbon dioxide, oxygen, and nitrogen, is transferred to the burette, accurately measured, by reading immediately, to prevent the absorption of carbon dioxide, and carbon dioxide and oxygen determined in the usual way.

Calculation. (*a*) *Hinman's Method.* 56.2 cc. of gas remained after the absorption; 77.4 cc. of oxygen were introduced, giving a total volume of 133.6 cc.

Residue after explosion	46.9 cc.
Residue after CO_2 absorption	28.2
Carbon dioxide formed	18.7
Contraction	133.6 − 46.9 = 86.7
Residue after O absorption	25.6
Oxygen in excess	28.2 − 25.6 = 2.6

[1] Bunsen, "Gasometrische Methoden," 2d ed., 73, 1877.
[2] Hempel, "Gas Analytische Methoden," 3d ed., 245, 1901.

The explosion of marsh gas or methane is represented by the equation

$$\boxed{CH_4} + \boxed{O_2}\ \boxed{O_2} = \boxed{CO_2} + \boxed{H_2O} + \boxed{H_2O}.$$

From this it is evident that the volume of carbon dioxide is equal to the volume of methane present; therefore in the above example, in the 56.2 cc. of gas burned, there were 18.7 cc. methane.

The total contraction is due (1) to the disappearance of oxygen in combining with the hydrogen of the methane, and (2) to the union of the free hydrogen with oxygen. The volume of the methane having been found, (1) can be ascertained from the equation above, equals twice the volume of the methane; hence

$$86.7 - (2 \times 18.7) = 49.3 \text{ cc.},$$

contraction which is due to the combustion of hydrogen. This takes place according to the following reaction:[1]

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{H_2O} + \boxed{H_2O}.$$

Hydrogen then requires for its combustion half its volume of oxygen, hence this 49.3 cc. represents a volume of hydrogen with $\frac{2}{3}$ its volume of oxygen, or $\frac{2}{3}$ volumes; hence the volume of hydrogen is 32.9 cc.

(*b*) *Hempel's Method.* Of the 82 cc. of gas remaining after the absorptions, 13.2 cc. were used for the explosion; 86.4 cc. air introduced, giving a total volume of 99.6 cc.

Residue after explosion	78.0 cc.
Residue after CO_2 absorption	73.2
Carbon dioxide formed	4.8
Contraction $99.6 - 78.0 =$	21.6
Residue after O absorption	70.2
Oxygen in excess $73.2 - 70.2 =$	3.0

The carbon dioxide being equal to the methane present, in the 13.2 cc. of gas burned there were 4.8 cc. of methane. The volume of methane is found by the proportion $13.2 : 82 :: 4.8 : x$, whence $x = 29.8$ cc.

The hydrogen is calculated similarly.

Another method for the estimation of hydrogen is by absorption with palladium sponge;[2] it, however, must be carefully prepared, and it is the author's experience that one cannot be sure of its efficacy when it is desired to make use of it. A still better absorbent of hydrogen[3] is a 1% solution of palladous chloride at 50° C.; when fresh this will absorb 20–50 cc. of hydrogen in ninety minutes. A proportionately longer time is required if more hydrogen be present or the solution nearly saturated. The methane could then be determined by explosion or by mixing with air and passing to and fro over a white-hot platinum spiral in a tubulated pipette called the grisoumeter[4] (grisou = methane).

Nitrogen. There being no direct and convenient method for its estimation with this apparatus, the percentage is obtained by finding the difference between the sum of all percentages of the gases determined and 100%.

[1] H_2O being as steam at 100° C. At ordinary temperatures this is condensed, giving rise to "total contraction."

[2] Hempel, Berichte, 12, 636 and 1006, 1879.

[3] Campbell and Hart, Am. Chem. J., 18, 294, 1896.

[4] Winkler, Fres. Zeit., 28, 269 and 288.

New[1] determined nitrogen in illuminating gas directly after the method of Dumas in organic substances; 150 cc. of gas are used, the hydrocarbons partially absorbed by fuming sulphuric acid and the remainder burned in a combustion tube with copper oxide; the carbon dioxide is absorbed and the residual nitrogen collected and measured.

Accuracy and Time Required. For the absorptions the apparatus is accurate to 0.1 cc.; for explosions by Hinman's method[2] the methane can be determined within 0.2%, the hydrogen within 0.3%; by Hempel's method within 1% for the methane and 7.5% for the hydrogen. The time required for the analysis of illuminating gas is from three to three and one-half hours; for air, from fifteen to twenty minutes.

NOTES. The object in filling the capillaries of the explosion pipettes with water or mercury before the explosion is to prevent the bursting of the rubber connectors on them. With mercury this is effected by introducing it through the T-joint in the connector. After testing for oxygen with the pyrogallate a small quantity of dilute acetic acid is sucked into the burette to neutralize any alkali which by any chance may have been sucked over into it. The acid is rinsed out with water and this is forced out by mercury before the burette is used again.

The water in the burette should be saturated with the gas which is to be analyzed —as illuminating gas—before beginning an analysis. The reagents in the pipettes should also be saturated with the gases for which they are not the reagent. For example, the fuming sulphuric acid should be saturated with oxygen, carbon monoxide, methane, hydrogen, and nitrogen; this is effected by making a blank analysis, using illuminating gas.

The method of analysis of the residue after the absorptions have been made by explosion is open to two objections· 1st, the danger of burning nitrogen by the violence of the explosion; and 2d, the danger of breakage of the apparatus and possible injury to the operator. These may be obviated by employing the apparatus of Dennis and Hopkins,[3] which is practically a grisoumeter with mercury as the confining liquid; or that of Jaeger,[4] who burns the gases with oxygen in a hard-glass or quartz tube filled with copper oxide. By heating to 250° C. nothing but hydrogen is burned; higher heating of the residue burns the methane. Recent work shows this procedure to be very slow and not very accurate. Or the mixture of oxygen and combustible gases, bearing in mind the ratio mentioned at the bottom of page 703, can be passed to and fro through Drehschmidt's[5] capillary heated to a bright redness. This consists of a platinum tube 20 cm. long, 2 mm. thick, 1.7 mm. bore, filled with three platinum or palladium wires. The ends of the tube are soldered to capillary brass tubes and arranged so that these can be water cooled. It is inserted between the burette and a simple pipette, mercury being the confining liquid in both cases. The air contained in the tube can be determined as in the case of the tube containing iodic anhydride, page 704.

To the method of explosion by the mixture of an aliquot part of the residue with air, method (*b*), there is the objection that the carbon dioxide formed is measured over water in a moist burette, giving abundant opportunities for its absorption, and that the errors in analysis are multiplied by about six, in the example by $\frac{210}{132}$.

[1] J. Soc. Chem. Ind., 11, 415, 1892.
[2] Gill and Hunt, loc. cit.
[3] J. Am. Chem. Soc., 21, 398, 1899.
[4] J. Gasbeleuchtung, 41, 764. Abstr. J. Soc. Chem. Ind., 17, 1190, 1898.
[5] Berichte, 21, 3242, 1888.

APPLICATIONS OF GAS ANALYSIS AND INTERPRETATION OF RESULTS

It is only within comparatively recent times that Gas Analysis has assumed any importance. The reasons are that the substances with which it deals are so intangible, the apparatus is complicated and fragile, and until lately, competition has not compelled manufacturers to seek every possible source of loss.

Some of its applications are to:

I. Chimney and flue gases;
II. Producer and fuel gases;
III. Illuminating gas;
IV. Sulphuric acid gases;
V. Mine gases;
VI. Electrolytic gases;
VII. Acetylene;
VIII. Atmospheric air.

I. CHIMNEY AND FLUE GASES

Here the object is to keep the carbonic acid (CO_2) as high as possible, and to avoid the formation of carbon monoxide: in large plants every additional per cent of carbonic acid means the saving of tons of coal. Savings of 20 to 33% by the use of gas analysis alone, have frequently come to the writer's notice. A satisfactory procedure is to post in the fire-room the percentage of carbonic acid obtained by each stoker, and stimulate a rivalry among the men—a bonus in the pay envelope is also effective. The determinations to be made are:

Analysis of Chimney Gases. Determination of carbon dioxide, oxygen, carbon monoxide, nitrogen, and in some case hydrocarbons. For this purpose the Orsat apparatus is widely employed: the hydrocarbons may be determined by the Hempel apparatus.

Usually a few determinations of carbonic acid will suffice, but for regular work the installation of some form of registering carbonic acid indicator should be installed.

Carbonic Acid Indicators.[1] These usually depend upon the principle of collecting 100 cc. of the gas, causing it to pass through a suitable absorber and collecting the residue in a bell which floats to a greater or less height according to the residual volume. The fluctuations of this bell are recorded after the usual manner of self-registering barometers or thermometers: the usual time for this analysis and record is five minutes.

By modifying this apparatus slightly, it can be applied to the determination of any absorbable gas as, for example, sulphurous acid or chlorine. It has been adapted to carbon monoxide absorption, but it is not usual or easy.

Haber[2] employs the refractive index of gases to determine the amount of carbonic acid in chimney gas; it gives results within half of 1%;[3] it has also been

[1] These can be obtained from the following: Combustion Appliance Co., Chicago; Precision Instrument Co., Detroit; Uehling Instrument Co., Passaic.
[2] Z. Ang. Chem., **19**, 1418, 1906; ibid., **23**, 1393, 1910.
[3] Mohr, ibid., **25**, 1313, 1912.

applied to other gaseous mixtures. The instrument is called the Interferometer or Gas Refractometer and is made by Zeiss of Jena.

The Determination of Temperature. This is done by inserting a thermometer, mounted in a metal tube, on the chimney side of the gas sampling tube. These resemble those used for determining steam temperatures or for "running" varnish. It should register to 360° and, under certain circumstances, one showing 550° may be desirable. A chemical thermometer with long stem may also be employed; it should never be inserted naked into the flue—as a sudden hot blast may break it—but always in a tube of cotton-seed oil or sea sand.[1] These thermometers should be tested for accuracy by comparison with a standard, in a carefully stirred oil bath. The standard should be kept exclusively for the purpose and be allowed to stay in the bath until cool. Sudden cooling of a thermometer changes the zero point. The standard can be certified by the makers or the United States Bureau of Standards.

Electric pyrometers are also of course available for these measurements. An error of five degrees (5°) in the reading of the thermometer affects the final result by about 20 calories.

In case none of these appliances be at hand, the maximum temperature can be determined by utilizing the melting-points of certain pure salts or metals; as tin 232°, bismuth 270°, cadmium 302°, lead 327°, zinc 419°, cadmium chloride 541°, antimony 630°, etc. These can be suspended in the chimney in small covered cast-iron boxes.

Composition of the Coal. This is determined by the usual methods of organic combustion and is required only for very accurate work.

Calculation:

a. Heat passing up chimney;

b. Pounds of air per pound of coal.

(*a*) *Heat Passing up Chimney.* The accurate calculation resolves itself into finding what volume of gas of the composition determined by analysis would be produced by a kilo of the coal used, and whose analysis is known. The temperature of the escaping chimney gases being also known, and their specific heat, the quantity of heat they carry off can be calculated: this divided by the calorific power of the coal gives the per cent of heat lost in the chimney gases. The calculation is rather long and will be found in detail in the author's book.[2]

The formula of Shields.[3]

$$\text{Per cent heat lost} = \frac{\text{Per cent carbon in coal}}{\text{Heating value of coal}} \times \frac{200 + \text{per cent } CO_2}{\text{Per cent } CO_2 + \text{per cent CO}} \times \text{rise in temperature in °C.} \times 0.2864,$$

gives results usually 0.5% low, as no cognizance has been taken of the water vapor.

Another formula[4] in which only the carbon dioxide and its temperature enters was proposed by Bunte and gives close results.

For every per cent of carbonic acid present 43.43 calories per cubic meter of

[1] With *rounded* grains, not river sand, as it would make scratches.
[2] "Gas and Fuel Analysis for Engineers." Wiley.
[3] "Power," **30**, 1121, 1909.
[4] J. J. Gasbeleuchtieng, **43**, 637, 1900.

flue gases have been developed = W; C = specific heat of the flue gases per cubic meter; then W/C represents the initial temperature (which is never attained) the ratio of which to the actual exit temperature of the flue gases shows the heat lost. If T = this initial temperature and t the rise of temperature of the flue gases, then t/T represents the heat lost in the chimney gases.

The following table gives the data for the calculation for both pure carbon and coal of average value:

Per Cent of CO_2 in Chimney Gas.	Specific Heat of Chimney Gas.	Initial Temperature, W/C. Degrees C.		
		For Carbon = T.	For Coal = T.	Diff. for 0.1% CO_2
1	0.308	141	167	
2	0.310	280	331	16
3	0.311	419	493	16
4	0.312	557	652	16
5	0.313	694	808	15
6	0.314	830	961	15
7	0.315	962	1112	15
8	0.316	1096	1261	15
9	0.318	1229	1407	15
10	0.319	1360	1550	14
11	0.320	1490	1692	14
12	0.322	1620	1830	14
13	0.323	1750	1968	14
14	0.324	1880	2102	13
15	0.324	2005	2237	13
16	0.325	2130	2366	13

If there were 11.5% carbonic acid, the initial temperature T would be 1762°; the rise of temperature in the chimney gases is 250°, the loss is $\frac{250}{1762}$ or 14.2%. The accurate calculation gives 14.1.

Finally, for very rapid work, Bunte's Chart, Table V, may be used. The results are within 2% for about 12% of carbonic acid. It is used by noting the point where the diagonal line representing CO_2 cuts the ordinate of temperature—the abscissa corresponding to this point represents the per cent loss.

The following table shows roughly the excess of air, and per cent of heat lost in the chimney gases, their temperature being 518° F.

Per cent CO_2..	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Vol. air more than theory =1.0.....	9.5	6.3	4.7	3.8	3.2	2.7	2.4	2.1	1.9	1.7	1.6	1.5	1.4	1.3
Per cent loss of heat.....	90	60	45	36	30	26	23	20	18	16	15	14	13	12

If the oxygen be from 1.5% to 2% with the temperature of escaping gases at 400–500° F., the fires are too thick; if it be less than 8% they are too thin.

(*b*) *Pounds of Air per Pound of Coal.* This can be determined by calculating the ratio of carbon to oxygen in the carbonic acid and carbon monoxide and oxygen of the chimney gases, or by the formula of Shields.[1]

[1] Loc. cit.

$$\text{Pounds of air per pound of coal} = 2.31 \frac{\text{Per cent of carbon in coal}}{\text{Per cent } CO_2 + \text{per cent } CO}$$

Loss Due to Carbonic Oxide. For every gram of carbon burned to carbonic oxide there is a loss of 5.66 calories.

Smoke. For the determination of the amount of smoke in the chimney gases, use may be made of the Ringelmann smoke scale. This consists [1] of a series of rectangles $\frac{3}{4}$ in. $\times \frac{1}{2}$ in. filled with cross-hatching lines a greater or less distance apart, with which the density of the smoke can be compared. Or the Eddy smoke recorder [2] may be employed; this consists of a tube of standard length through which the smoke gases are drawn. A standard electric light is fixed at one end of the tube and viewed through the smoke; its density is measured by the extent to which the light is obscured.

II. PRODUCER AND FUEL GASES. BLAST-FURNACE GAS

Here the object is the reverse of that in the chimney gases, to keep the percentage of carbon monoxide as high as possible and, for gas-engine purposes, the per cent of hydrogen constant.

The determinations made are the same as in chimney gas—CO_2, O, CO, N, and oftentimes hydrogen and hydrocarbons; the quantity of *dust* is sometimes important. The heating value is determined as in illuminating gas, p. 713. The efficiency of conversion would be found by measuring the number of cubic feet of gas made per ton of coal gasified; the calorific power of each (gas and coal) being known, their quotient represents the efficiency. The heat contained in the gas due to its sensible heat, found after the manner of calculating the loss in chimney gases (i.e., volume gas $\times$ weight $\times$ rise of temperature $\times$ specific heat) is to be added to this for accurate work.

As showing producer gas practice, the following typical analyses are cited:

	Anthracite.[4]	Bituminous.[4]	Blue Water Gas.[4]	Lignite.[4]	Peat.[5]	Tan.[3, 4]	Wood.[5]
CO	27.0	27.0	45.0	22.0	30.6	14.2	13.3
H_2	12.0	12.0	45.0	9.6	6.1	8.7	21.0
CH_4	1.2	2.5	2.0	1.6	5.1	5.6	2.6
C_2H_4	.....	0.4	.....	0.7	.....	.....	0.3
CO_2	2.5	2.5	4.0	6.4	5.7	15.0	16.0
N_2	57.0	55.3	2.0	58.9	52.5	56.0	46.7
O_2	0.3	0.3	0.5	0.8	.....	0.4	0.1
B.t.u.	137	157	322	.....	.....	132	140

[1] Power, 40, 66.

[2] Made by the Hamler-Eddy Smoke Recorder Co., Chicago.

[3] With 38.7% H_2O, 3.2% ash.

[4] From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.

[5] Richards, J. W., J. Frank. Inst., 415, 1900, quoted from V. Ihering, "Gas Maschinen."

GAS FROM DIFFERENT KINDS OF PRODUCERS

	Down Draft.[3]	Up Draft.[3]	Suction.[1]	Pressure, Taylor.[1, 2]	Mond.[1]	Blast Furnace.[4]	Siemens[4]
CO	17.5	18.3	26.0	22–30	16.0	24	28
H_2	11.8	12.9	18.5	15–7	24.0	2	2
CH_4	1.1	3.1	0.5	3–1.5	2.2	.....	.....
C_2H_4	.04	0.2	.....	.....	.....	2	2
CO_2	9.2	9.8	8.0	6–1.5	12.4	12	3
N_2	60.1	55.6	47.0	54–60	45.4	60	65
O_2	0.2	.04	.....	.....	0.	.....	.....
B.t.u.	110	.....	145	138	146	106	122

Determination of Dust. Liddell[5] recommends the following: lump sugar is crushed, and that which is retained by a 90-mesh sieve packed in a 2-in. layer upon copper or brass gauze contained in a glass tube. The sugar is slightly moistened and the gas sucked through it: it is then dissolved in water and the dust collected upon a tared Gooch crucible and weighed. Another procedure and apparatus recommended by the Sargent Steam Meter Co., of Chicago,[6] consists in sucking the gas through a diaphragm consisting of a weighed filter 4½ ins. in diameter, drying and noting the increase in weight.

III. ILLUMINATING GAS

The determinations usually made are as follows:

a. Candle power;
b. Calorific power;
c. Sulphur;
d. Ammonia;
e. Analysis;
f. Carbon dioxide;
g. Specific gravity;
h. Tar.

(a) **Candle Power.** This can be very satisfactorily found using a 60-in. open-bar photometer and Leeson contrast disc. The gas should be burned from a burner commercially obtainable which gives the highest candle power; for gas from 14 to 21 candle power, Sugg's London argand burner, sizes C to F, should be used; for richer gases, Sugg's table top or the Bray slit burner. For a standard of comparison, the sperm candle is convenient, satisfactory, and very extensively used: the Elliott kerosene and Hefner amyl acetate lamps are also employed.

For accurate work the Lummer-Brodhun disc and electric standards, or the Hefner lamp should be used. For the determination of candle power, reference

[1] From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.
[2] With anthracite buckwheat.
[3] "Résumé of Producer Gas Investigations," Bureau of Mines Bulletin 13, Fernald & Smith.
[4] Richards, J. W., J. Frank. Inst., 415, 1900, quoted from V. Ihering, "Gas Maschinen."
[5] Power, 38, 93.
[6] Power, 27, 331.

may be had to Circular No. 48 of the Bureau of Standards on "Standard Methods of Gas Testing," 1914, or Stone, "Practical Testing of Gas and Gas Meters," Wiley, 1909.

Carburetted water gas shows from 20–28 candle power, coal gas 14–20, oil gas 45–60, oil-air gas 30–35, gasolene 12–17, acetylene 170–200. (Stone, op. cit.)

(b) **Calorific Power.** (*a*) *Direct Determination.* This is most commonly

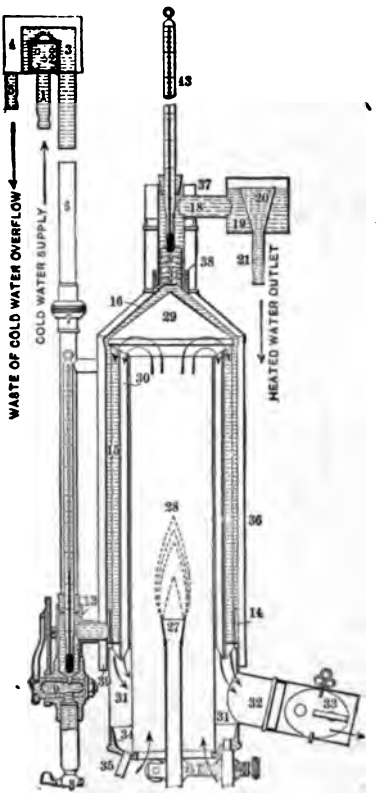


FIG. 124.

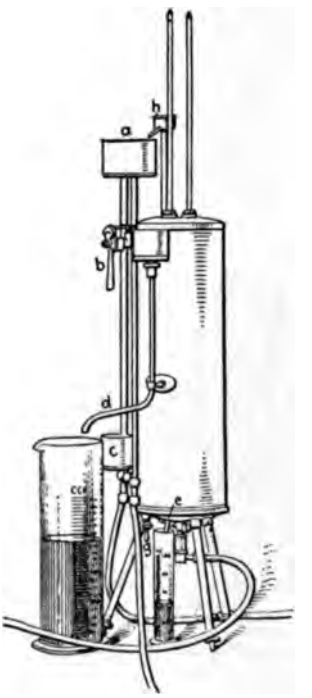


FIG. 125.

determined by the Junkers calorimeter, although others in use are the Sargent, Doherty, and in England the Boys and Simmance-Abady.

The original form is shown in section in Fig. 124 and the later modification in Fig. 125. As seen in Fig. 124 it consists of a combustion-chamber, 28, surrounded by a water-jacket, 15 and 16, this being traversed by a great many tubes. To prevent loss by radiation this water-jacket is surrounded by a closed annular air-space, 13, in which the air cannot circulate. The whole apparatus is constructed of copper as thin as is compatible with strength. The water enters the jacket at 1, passes down through 3, 6, and 7, and leaves it at 21, while the hot combustion gases enter at 30 and pass down, leaving at 31. There is therefore

not only a very large surface of thin copper between the gases and the water, but the two move in opposite directions, during which process all the heat generated by the flame is transferred to the water, and the waste gases leave the apparatus approximately at atmospheric temperature. The gas to be burned is first passed through a meter, Fig. 126, and then, to insure constant pressure, through a pressure-regulator. The source of heat in relation to the unit of heat is thus rendered stationary; and in order to make the absorbing quantity of heat also stationary, two overflows are provided at the calorimeter, making the head of water and over-

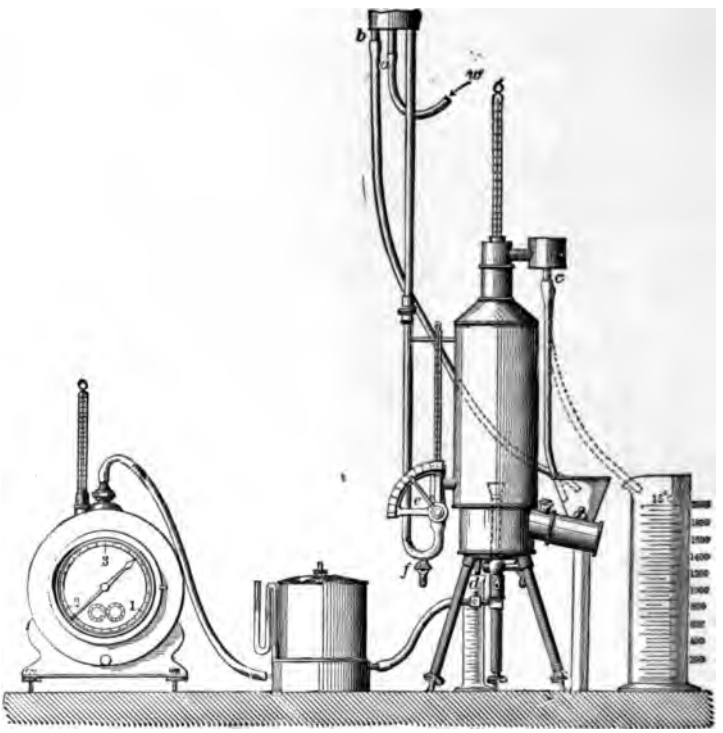


FIG. 126.

flow constant. The temperatures of the water entering and leaving the apparatus can be read by 12 and 43; as shown before, the quantities of heat and water passed through the apparatus are constant. As soon as the flame is lighted, 43 will rise to a certain point and will remain nearly constant.

Manipulation. The calorimeter is placed as shown in Fig. 126, so that one operator can simultaneously observe the two thermometers of the entering and escaping water, the index of the gas-meter, and the measuring-glasses.

No draft of air must be permitted to strike the exhaust of the spent gas.

The water-supply tube *w* is connected with the nipple *a* in the center of the upper container; the other nipple, *b*, is provided with a waste-tube to carry away the overflow, which latter must be kept running while the readings are taken.

The nipple *c*, through which the heated water leaves the calorimeter, is connected by a rubber tube with the large graduate. *d* empties the condensed water into the small graduate.

The thermometers being held in position by rubber stoppers and the water turned on by *e* until it discharges at *c*, no water must issue from *d* or from 39, Fig. 19, as this would indicate a leak in the calorimeter.

The cock *e* is now set to allow about two liters of water to pass in a minute and a half, and the gas issuing from the burner ignited. Sufficient time, about twenty minutes, is allowed until the temperature of the inlet-water becomes constant and the outlet approximately so; the temperature of the inlet-water is noted, the reading of the gas-meter taken, and at this same time the outlet-tube changed from the funnel to the graduate. Ten successive readings of the outflowing water are taken while the graduate (2-liter) is being filled and the gas shut off.

A better procedure is to allow the water to run into tared 8-liter bottles, three being used for a test, and weighing the water. The thermometer in the outlet can then be read every half-minute.

Example.—Temp. of incoming water, 17.2°
Temp. of outgoing water, 43.8°
Increase, 26.6°

Gas burned, 0.35 cu.ft.

$$\text{Heat} = \frac{\text{Liters water} \times \text{Increase of temp.}}{\text{Cu.ft. gas}} = \frac{2 \times 26.6}{0.35} = 152.3 \text{ C.}$$

From burning 1 cu.ft. of gas 27.25 cc. of water were condensed. This gives off on an average 0.6 C. per cc.

$27.25 \times 0.6 = 16.3$ C.; $152.3 - 16.3 = 136$ C. per cubic foot; $136 \times 3.968 = 540$ B.t.u.

NOTES. After setting up the apparatus the *first* thing to be done is to turn on the *water*—(*not the gas*). Similarly, the *water* should be shut off *last*. All connections and the meter should be tested for leaks before each test. The water level in the meter should be checked daily. Slight drafts caused by moving suddenly near the apparatus will vary outlet readings and vitiate the test. The instrument should not be set up near a window or heating apparatus where radiant heat might affect the readings.

If 0.2 cu.ft. of gas are burned, then an error of 0.1° F. in temperature of water means an error of 4 B.t.u.; an error of 0.01 lb. water, 0.9 B.t.u.; 1° F. in gas temperature, 1.8 B.t.u.; 0.1 in. (barometer), 2 B.t.u.; 1 in. water pressure of gas, 1.5. B.t.u.[1]

The calorific power obtained without subtracting the heat given off by the condensation of the water represents the *total* heating value of the gas. This is the heat given off when the gas is used for heating water or in any operation where the products of combustion pass off below 100° C. The *net heating value* represents the conditions in which by far the greater quantity of gas is consumed, for cooking, heating and gas engines, and is one which should be reported. It should, however, be corrected,[2] to the legal cubic foot, that is, measured at 30 ins. barometric pressure, and 60° F. saturated with moisture.

The apparatus has been tested for three months in the German Physical Technical Institute with hydrogen, with but a deviation of 0.3% from Thomson's value. This

[1] Rept. Joint Committee on Calorimetry Public Service Commission and Gas Corporations in the Second Public Service District of New York State, p. 81, 1910.

[2] A difference of 1° C. or of 3 mm. pressure makes a change of 0.3% in the volume. Pfeiffe, J. Gasbeleucht., **50**, 67, 1907.

value may vary nearly that amount from the real value owing to the method which he employed.

The chief sources of error are,[1] in adjusting the meter, in measuring the temperature—rise of the water, and in changing over the outflow water to the weighed vessels.

(*b*) *By Calculation.*[2] Let us suppose an illuminating gas gave the following analysis: Illuminants 15, carbon monoxide 25.3, methane 25.9, hydrogen 27.9%; the heating value of these gases according to Table 3, page 737 is as follows:

$$\begin{aligned} 0.15 \times 2000 &= 300.0 \text{ B.t.u.} \\ 0.253 \times 341 &= 86.3 \\ 0.259 \times 1065 &= 276.0 \\ 0.279 \times 345 &= 96.3 \\ \hline & 758.6 \text{ B.t.u.} \end{aligned}$$

which is the gross heating value of the gas. The correction for the heat lost is found as with chimney gases, by multiplying the volume of the combustion gases by their weight × specific heat × rise of temperature.

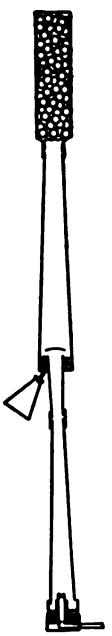


FIG. 127.

(c) **Sulphur.** Sulphur, being present in gas in so many forms, is determined by combustion and usually reported in grains of sulphur per hundred cubic feet.

One of the most easily portable and satisfactory forms is that of Hinman and Jenkins described as follows:[3] The upper vessel, Fig. 127, is a "bead glass" 300 mm. long and 60 mm. in diameter; this is filled with large cut-glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm. long and 50 mm. lower internal diameter. To the upper adapter is attached, by means of the "connecting piece," the lower adapter, 400 mm. long and 40 mm. lower diameter. The connecting piece projects 12 mm. above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm. hole; surrounding the burner is a glass tube 20 mm. in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm. in diameter. Into this chamber, which serves to contain 10% ammonium hydroxide, the lower adapter dips 10 mm.

The lower adapter is joined to the "connecting piece" by a short cork-lined metal tube. Although radically different in form, this apparatus is very similar to the Referees' in general principle and in method of use, the principal difference

[1] Technologic Papers of the Bureau of Standards No. 36. "Gas Calorimetry," Waidner and Mueller, page 100, 1914.

[2] U. S. Geol. Survey Paper No. 48; Part III, page 1005.

[3] Jenkins, J. Am. Chem. Soc., 28, 543, 1906, also Technologic Paper No. 20, Bureau of Standards, McBride and Weaver "Determination of Sulphur in Illuminating Gas," 1913, also Stone, op. cit.

being the use of ammonium hydroxide instead of dry ammonium carbonate as a source of ammonia. About 10 cc. of concentrated ammonium hydroxide is placed in the reservoir about the burner at the beginning of the test and about 5 cc. more added every fifteen or twenty minutes. The gas is consumed at the rate of 0.4 to 0.6 cu.ft. per hour, and 2.5 to 3 ft. burned, if the sulphur is to be estimated gravimetrically, otherwise 1 cu.ft. is enough. When the run is completed the apparatus is allowed to cool and is then flushed four times by pouring 50 cc. portions of water in at the top of the bead tube. To the solutions and washings are added 2–3 cc. bromine water, and it is evaporated to 30 or 40 cc.; an excess of a hydrochloric acid solution of barium chromate is added to the hot solution, it is gently boiled, an excess of dilute ammonia added, again boiled for a minute, filtered and washed. The ammonium chromate in the filtrate (the chromic acid being equivalent to the sulphuric acid in the original solution) after being boiled in a stout flask, with a Bunsen valve, to expel the air, is cooled and titrated directly with stannous chloride (3.25 grams Sn per liter) using starch and potassium iodide to accentuate the end point.

The equations are:

$$(NH_4)_2SO_4+BaCrO_4=BaSO_4+(NH_4)_2CrO_4,$$

$$2(NH_4)_2CrO_4+2HCl=(NH_4)_2Cr_2O_7+2NH_4Cl+H_2O,$$

$$3SnCl_2+(NH_4)_2\,Cr_2O_7+14HCl=3SnCl_4+2NH_4Cl+2CrCl_3+7H_2O.$$

The strength of the stannous chloride should be determined at the same time by standard bichromate of potassium.

Or the sulphuric acid can be determined with the turbidimeter as for sulphur in oils, page 570. The amount of sulphur is usually from 20 to 30 grains per 100 cu.ft.

Sulphuretted Hydrogen.[1] The test is made by hanging a strip of paper moistened with lead acetate solution (1 : 20) in a bell-jar or tube through which the gas is passing at about 5 cu.ft. per hour and allowing it to act for one minute. Usually several tests are made. The gas should be taken fresh from the main and care should be taken not to confound any black tarry spots with lead sulphide. A properly purified gas should give no test.

It is quantitatively determined by drawing a known volume of the gas through standard iodine solution. Tutweiler[2] measures the gas in a modified Bunte burette over mercury, and having added starch solution, runs in a known quantity of standard iodine solution until it is in slight excess. If 100 cc. of gas were taken, the number of cubic centimeters of solution gives the grains of H_2S per 100 cu.ft., 1 cc. iodine = 0.0017076 gram iodine = 100 grains H_2S per 100 cu.ft.

(d) Ammonia. This is determined by absorption in standard acid colored with cochineal: 10 cc. of HCl are placed in the bulb, Fig. 117, 2–3 drops cochineal solution added, and the gas allowed to bubble through it until the yellow color changes to a deep purple; the meter is now read. The acid is made by diluting 38.2 cc. N/10 HCl to 1 liter, 10 cc. = 0.01 grain of NH_3; the cochineal solution is made by treating 3 grams of the ground insect with 250 cc. 20% alcohol, allowing to stand forty-eight hours and filtering. The bubble tube is inserted in series

[1] Tech. Paper No. 41, Bureau of Standards, "Lead Acetate Test for Hydrogen Sulphide in Gas."

[2] J. Am. Chem. Soc., **23**, 173, 1901.

with the gas supply to the sulphur apparatus, Fig. 127, (c) so that both determinations are run at one time: the gas is passed through at the rate of 0.6 to 0.8 cu.ft. per hour. Massachusetts law limits the amount of ammonia to 10 grains per 100 cu.ft.

(e) **Analysis.** The volumetric analysis is carried out according to pages 704: either bromine water or fuming sulphuric acid can be used to absorb the "illuminants." Besides ethylene, it may be desirable to determine benzol: this is best done according to Dennis, O'Neill and McCarthy [1] by absorption in an ammoniacal solution of nickel cyanide.

Naphthalene. This is determined in purified gas by passing it through N/20 picric acid solution. White [2] determines it in raw gas by precipitation of the picrate and subsequent recovery of the naphthalene.

COMPOSITION OF COMMERCIAL GASES [3]

	CO_2	Ill'ts.	O_2	CO.	H_2	CH_4	C_2H_6	N_2	Candle Power.	B.t.u.
Coal	1.6	4.0	0.4	8.5	49.8	29.5	3.2	3.2	16.1	622
Carb. water	3.0	13.3	0.4	30.4	37 7	10.0	3.2	2.1	22.1	643
Blue water	3.4	0.0	0.9	40.9	50 8	0.2	0.	3.5	.....	299
Pintsch	0.2	30.0	0.	0.1	13 2	45.0	9.0	1.6	43.0	1276
Blau	0.	51.9	0.	0.1	2.7	44.1	0.	1.2	48.2	1704
Oil-water	2.6	7.0	0.2	9.2	39.8	34.6	....	6.6	19.7	680
Oil	0.3	31.3	0.	2.4	13.5	46.5	3.9	1.1	38.0	1320
Gasolene	..	1.5	18.5	..	..	C_6H_{14}	=10.3	69.7	16.0	514
Acetylene	..	96.0	0.8	..	..	....	....	3.2	225.0	1350
Natural	0.3	0.3	0.3	0.5	2.3	92.6	....	3.5	$\frac{H_2S}{0.2}$	840–1170[4]

(f) **Carbon dioxide.** This is best determined by Rudorff's method [5] which consists in titrating about a liter of the gas with standard potassium hydroxide. The arrangement and manipulation of this apparatus will be evident from Fig. 128: the capacity of the Woulff bottle must be known and if the gas contains hydrogen sulphide, it must be absorbed by passage over manganese dioxide.

(g) **Specific Gravity.** The readiest method depends upon the time of efflux of the gas compared with air; sp.gr. $= \frac{G_1}{A_1} G$ and A represent the times of efflux in seconds of gas and air. The apparatus is obtainable from the dealers, or may be constructed according to Jenkins [6] as follows:

"It consists, Fig. 129, of two large rubber stoppers, each having a brass tube, projecting laterally near the large end, and connecting with the hole in the stopper. A glass piece A in the form of a truncated cone fits tightly over one stopper; it is 9 ins. long, 1½ ins. diameter at the base and 1 in. at the top. A similarly shaped piece B 9 ins. long by 1½ ins. diameter at the lower end fits over the second stopper: 2 ins. above the latter the tube has a constriction 1 in. in diameter, and at its

[1] J. Am. Chem. Soc., 30, 236, 1908.
[2] Proc. Mich. Gas Association, 83, 1904, 1905.
[3] Fulweiler, Rogers' and Aubert's, "Industrial Chemistry," 2d Ed., 404.
[4] Orton, Geol. of Ohio, VI, 137.
[5] Hempel, op. cit., 262.
[6] Stone, op. cit., 261.

upper part is narrowed to a neck $\frac{5}{16}$ in. in diameter which is ground on the inside to receive the end of a tube $7\frac{1}{2}$ ins. long and $\frac{1}{4}$ in. in diameter, in the upper end of which is fitted a platinum plate containing the emission orifice. One and three-fourths inches below this plate is a three-way glass stopcock, and 3 ins. below the latter a scratch surrounds the tube and serves as the upper mark in the escape of the gas.

"Fitted into the hole in the stopper is a hollow cylinder of brass to which is soldered a curved piece of brass wire pointed at the end, which rises $1\frac{1}{2}$ ins. above the surface of the stopper. The two brass tubes projecting from the outside of the stoppers are joined by a piece of rubber tubing 15 to 18 ins. long.

"In using this instrument the larger tube *B* is filled with water, of the temperature of the room, nearly to the top, the stopcock being turned so that egress

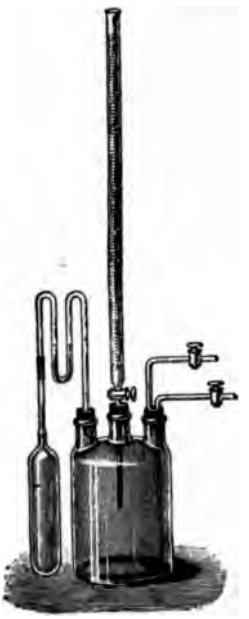


FIG. 128.

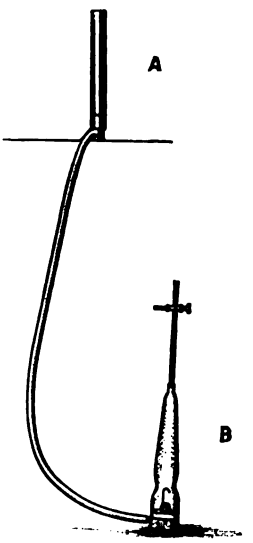


FIG. 129.

of air from the smaller tube is prevented. The larger tube is placed on an elevated surface just high enough so that its bottom is above the level of the scratch on the narrow outlet tube, the cock is turned so that the air may escape through the orifice in the platinum plate, and on the second, when the point of the brass wire breaks the surface of the rising water, a stop watch is started. The latter is stopped when the water exactly reaches the scratch.

"The large tube is lowered, and the stopcock turned so that air may enter through its hollow point. When the water is again all in the large cylinder, the cock is turned to connect the small vessel with the outside air through the platinum tip, the large cylinder is replaced on the elevation and the operation repeated. Results should be obtained which check within one-fifth second.

"Now connect a rubber tube to the gas supply and to the tip of the stopcock, lower the large cylinder and force the water into the latter by means of the gas pressure. Thoroughly saturate the water with the gas to be tested; this may be done by shaking gas and water together and by forcing the water up and down in the small vessel in contact with the gas. Repeat the operation with gas in in the same manner as described for air. The calculation is made in accordance with the formula.

"The advantages of this apparatus are its portability, its cheapness, its rapidity and accuracy. When set up, the cylinders are inclined to be a trifle unstable; this may be overcome by fastening a lead plate to the base of each stopper. Four precautions in connection with its use should be emphasized: (1) The water must be of the room temperature; (2) the water must be thoroughly saturated with the gas; (3) the platinum tip, stopcock, and upper part of the tube must be kept dry and clean; (4) the large cylinder must always, in any one determination, be placed at the same height."

Another method consists in the use of the Lux gas balance. This consists of a balanced globe into which the gas previously filtered through cotton, passes and its specific gravity is read off directly on a scale.

The knowledge of the specific gravity is important, as it is involved in the formula for the calculation of the flow of gas in pipes; it also enables the gas manager to ascertain the weight of gas produced from the coal, and to get an idea of the nature and amount of impurities in the gas, all these being heavier.

(h) **Tar.** For the estimation of tar, Clemens Winkler [1] recommends the procedure of Tieftrunk: This consists in passing the gas through 25% alcohol and collecting and weighing the tar on a tared filter.

IV. SULPHURIC ACID GASES

or more accurately the gases involved in the manufacture of sulphuric acid:

a. Burner gases;
b. Nitrogen gases;
c. Oxygen;
d. Gases involved in the contact process.

(a) Burner Gases. Sulphur Dioxide

This gas may be determined by the method of Reich. It consists in aspirating the gas through standard iodine solution (N/10 is suitable) until it is decolorized. The amount of iodine used in the test and the volume of the aspirated gas being known, the percentage of SO_2 can readily be calculated.

Fig. 130 shows a form of apparatus for making this determination. The standard iodine, 5 to 25 cc. N/10 I, diluted to 150 to 200 cc., is placed in the two-necked Woulff bottle and starch indicator added.[2] The gas to be tested is aspirated through the iodine until the color of the starch blue fades completely. Water which flows out from the separatory funnel *B*, connected with the Woulff bottle, produces the suction, and the amount measures the volume of the aspirated gas.

[1] "Die Industrie Gase," page 52, also Hempel, op. cit., 239.

[2] Starch indicator may be omitted if the light is good for observing the fading out of the iodine color.

From the quantity of iodine used and the volume of the gas required to decolorize the solution the per cent of sulphur dioxide is calculated.

In place of the Woulff bottle an ordinary 500-cc. wash bottle with a two-hole rubber stopper will do. The flask is shaken during the aspiration of the gas.

In making tests of gas rich in SO_2, 25 cc. of tenth normal iodine should be taken, and smaller amounts for gases poor in the oxide.

The Reich method is more applicable for determining small amounts of SO_2. A 12–15-liter graduated aspirating bottle is used in works tests of exit gases for measuring the gas. Since these volumes are under standard conditions (760 mm. and 0° C.), it will be necessary to convert the volumes obtained in the tests to these conditions, using the formula $V = V^\circ \frac{P^\circ - w}{760\,(1+0.00367t)}$ where V° = measured volume, P° = observed barometric pressure, t = temperature of the gas, and w = aqueous vapor pressure at temperature of the test.

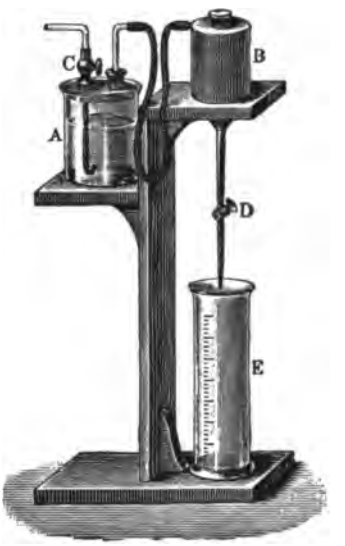


FIG. 130.

TABLE FOR REICH'S TESTS FOR PERCENTAGE SO_2. USING TENTH NORMAL IODINE SOLUTION

Volume Per cent SO_2	25 cc. N/10 Iodine.	10 cc. N/10 Iodine.	5 cc. N/10 Iodine.
12	205 cc. gas	.....	.....
11.5	215 " "	.....	.....
11	226 " "	.....	.....
10.5	238 " "	.....	.....
10	252 " "	.....	.....
9.5	265 " "	.....	.....
9	283 " "	.....	.....
8.5	300 " "	.....	.....
8	321 " "	.....	.....
7.5	344 " "	.....	.....
7	371 " "	148 cc. gas	.....
6.5	402 " "	161 " "	.....
6	438 " "	175 " "	.....
5.5	.....	192 " "	.....
5	.....	212 " "	.....
4.5	.....	237 " "	.....
4	.....	268 " "	.....
3.5	.....	308 " "	154 cc. gas
3	.....	361 " "	181 " "
2.5	.....	436 " "	218 " "
2	.....	.....	274 " "
1.5	.....	.....	367 " "
1.4	.....	.....	393 " "
1.3	.....	.....	424 " "
1.25	.....	.....	442 " "

Sulphur Dioxide in Exit Gases.[1] Sulphur dioxide is seldom above 1% in exit gases leaving the absorption tower of the sulphuric acid plant. Generally the loss is below 0.2% on a carefully regulated unit. The Reich method is sufficiently accurate for this determination, for all practical purposes. If 10 cc. of N/10 iodine are used the percent SO_2 may be calculated by the formula:

$$\frac{11.17}{V_0+11.17}=\%SO_2.$$

V_0 = volume of the gas reduced to standard condition 0° C and 760 mm.
11.17 = cc. of SO_2 gas equivalent to 10 cc. of N/10 iodine.

The following table is calculated on the assumption that the gas is under a pressure of 760 mm. + vapor pressure of 17 mm., at room temperature of 20° C.

Measured Vol.	Per cent SO_2	Measured Vol.	Per cent SO_2
1000 cc	1.22	3200 cc	.38
1100 cc	1.09	3400 cc	.36
1200 cc	1.01	3600 cc	.34
1300 cc	.93	3800 cc	.32
1400 cc	.87	4000 cc	.31
1500 cc	.81	4200 cc	.29
1600 cc	.76	4400 cc	.28
1700 cc	.72	4600 cc	.27
1800 cc	.67	4800 cc	.26
1900 cc	.64	5000 cc	.25
2000 cc	.61	5500 cc	.22
2100 cc	.58	6000 cc	.20
2200 cc	.55	6500 cc	.18
2300 cc	.53	7000 cc	.17
2400 cc	.51	7500 cc	.16
2500 cc	.49	8000 cc	.15
2600 cc	.47	8500 cc	.14
2700 cc	.45	9000 cc	.14
2800 cc	.44	9500 cc	.13
2900 cc	.42	10000 cc	.12
3000 cc	.41		

Sulphur Dioxide in the Inlet Gases of the Sulphuric Acid Contact System[1]

Apparatus. *Burette.* This should be of the bulb type with a graduated capacity of 100 cc., the bulb holds about 87 cc.; the stem is graduated in tenths of a cubic centimeter from 0 to 12 cc. The diameter of this graduated portion is such that each cubic centimeter occupies approximately 18 mm. in length. The total length of the burette is 45 to 50 cc.

There is a constriction at the lower end of the burette, or the rubber tube connecting the burette with the leveling tube may be pinched down so that it requires 10 to 15 seconds to pass 100 cc. of mercury in or out of the burette.

The burette has a water jacket of sufficient capacity to include the chamber of the burette and its graduated portion. The diameter should be sufficient to accommodate the bulbed portion of the burette and a thermometer suspended by its side. Distilled water boiled free of air is used in this water jacket.

[1] Communicated by W. W. Scott.

thermometer registering from 5 to 35° graduated in tenths of a degree is uspended in the water jacket next to the bulb.

eveling Tube. This is preferably a straight glass cylinder constricted at · end to accommodate the heavy-walled rubber tubing, connecting the tube the burette. This tube is about 52 cm. long and has a diameter of 18 to m. The lower portion of the tube, where this is held by the hand, has a cover- ither of rubber, or of a heat-insulating material, to prevent warming of the ury while making the test.

apillary Tube. The tube connecting the burette with the pipettes and the

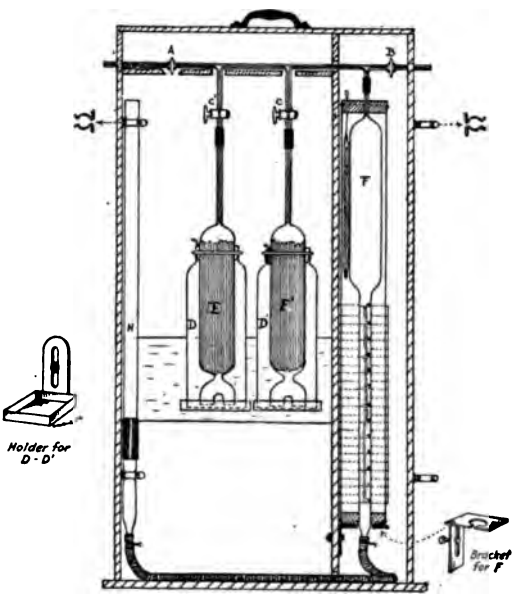


FIG. 131.[1]

ling pipe should have a fine capillary—the entire internal capacity should xceed 1 cc. Details of construction shown in the figure.

ipette. The cylinder of the pipette has a capacity of 150 to 175 cc. The te reservoir of 500 to 550 cc. capacity is recommended.

eagents. Mercury. Mercury is used in the measuring burette. This d be kept bright and clean and "drag no tail." To keep the gas saturated moisture the burette should contain about 0.2 cc. of distilled water over the ury.

'ater Solution of Chromic Acid. A 50% solution is recommended, although aker solution may be used. The strength of the reagent, however, should 'er 25% CrO_3.

ampling. The iron pipes carrying the gas to and from the testing appara ave a diameter of ½ in. to ¾ in. The line is run from the positive pressure

[1] Orsat apparatus modified by T L. Briggs and W. W. Scott

flue near the blower to the testing apparatus and back to the minus pressure flue entering the blower, and the gas allowed to flow continuously through this shunt line.

Making the Test. A volume of 100 cc. of the gas is drawn into the chamber burette (Fig. 131), by opening the stopcock *A* (*B* being closed) and lowering the leveling-tube—Stopcock *A* is closed, *B* opened and the gas expelled into the air by raising the leveling tube *H*, using care to prevent mercury bumping at the top of the reservoir. (Mercury carried into the chromic acid will reduce this reagent.) A second 100 cc. of the gas is taken and expelled as before. Finally a third 100 cc., carefully measured, is taken for the test. The top of the mercury columns in the burette and leveling tubes should be exactly level. The water surface should be at the 0 mark on the burette. Stopcock *B* is always closed during the drawing in of the gas. The temperature of the water jacket is now observed. Stopcock *A* is closed and stopcock *C* leading to the absorption pipette opened. The leveling tube is raised as before and the gas completely passed into the pipette. The gas is drawn back into the measuring burette by lowering the leveling tube and measured. The mercury columns should stand at the same level, the reading being taken at the surface of the water over the mercury. A second pass into the pipette is now made and, if no further contraction of the gas occurs, the reading taken. The temperature is observed and a correction made of 0.36 cc. per degree (centigrade) rise or fall of temperature. This correction is added if the temperature rises, or is subtracted if the temperature falls.

The contraction of the gas, due to absorption of SO_2, in terms of cc. gives the direct per cent reading.

Example:

100 cc. gas taken.
Final reading 91.5, i.e., direct = 8.5 cc.
Temperature change = 0.4° rise.
Then $8.5 + (.4 \times .36) = 8.6\%$ SO_2.

Tests should be made in duplicate, each Orsat having two pipettes. Very little more time is required to run the check test if the following method is observed. The first sample is taken and passed into one of the pipettes; a second sample, immediately taken, is passed into the second pipette. The first sample is now again measured and then returned to the first pipette and then the check sample measured and returned to its pipette. The first sample is again measured and if a further contraction is observed it is again passed into its pipette and the process repeated with the second sample. By thus alternating the tests and allowing the gas to stand in the pipettes the second pass will cause complete absorption of SO_2, third pass seldom being necessary.

Notes and Precautions. *Burette.* The constriction preventing a rapid flow of mercury accomplishes the following:

1. It prevents the wave motion of mercury, which results from a rapid flow. This wave motion makes it exceedingly difficult to draw in 100 cc. of gas accurately, and makes it necessary to hold the tube several seconds until the motion has ceased before taking a reading.

2. The constriction prevents mercury bumping into the capillary and from being thus carried into the absorption reagent.

3. It minimizes the danger of drawing the absorption reagent into the chamber burette.

Water in the Burette. The burette should, as stated, always contain about 0.2 cc. of water, over the mercury to saturate the gas with moisture. Results 1 to 4% low will be obtained if the burette is allowed to become dry, the amount of error depending upon the temperature of the gas. One hundred cc. of dry gas expand upon absorbing moisture to 101.2 cc. at 10°; 101.7 cc. at 15°; 102.3 cc. at 20°; 103.1 cc. at 25° and 104.1 cc. at 30°.

Leveling Tube. The covering recommended prevents warming of the mercury with the hand. When the apparatus is kept stationary, practically no change of temperature takes place during the test if the mercury is thus protected, so that a temperature correction will not be required. If the apparatus is moved from a warm to cold zone or vice versa, temperature corrections will become necessary.

Pipette. The form of pipette shown in the illustration is simple and compact. The bottle affords both protection and acts as a water jacket. The pipette is filled with thin-walled tubes having a small bore. The pipette should be tightly packed as loose packing and large-bored tubes both lessen the efficiency of the pipette, cutting down the surface for absorption.

Rubber Tube Connection. Since sulphuric anhydride acts on rubber, in presence of this gas, rubber tubing for connecting the testing apparatus to the sampling pipe should not be used, except in flush connections with the pipe in contact with the inlet tube of the apparatus. In absence of sulphuric anhydride the use of rubber tubing is not objectionable.

Cleaning the Burette upon Accidental Drawing in of Chromic Acid. Should the reagent be accidentally sucked into the capillary or into the burette, it may be easily washed out with distilled water by drawing this through stopcock *B* and flushing out several times by lowering and raising the leveling tube. The excess water may be removed from the capillary by opening stopcock *C* and allowing to flow out. If mercuric oxide is formed in the burette it may be dissolved by flushing with sodium hydroxide solution.

Chromic Acid Reagent. Theoretically, a charge of 50% aqueous chromic acid solution (100 g. CrO_3+100 g. H_2O) amounting to 300 cc., is sufficient to absorb the SO_2 of over 12,000 determinations. In practice, however, the reagent should be renewed long before the chromic acid has been used up by the sulphurous acid.

Number of Passes. Although two passes are generally sufficient to completely absorb the SO_2, it is necessary to make a third pass and observe whether any further contraction takes place. If the reagent is effective and there are no leaks in the apparatus the third pass will show no change.

Lubrication of Stopcocks. A mixture of beeswax and vaseline or wool grease (1 : 2) has been found excellent for this purpose. Not only does it lubricate the stopcock, but it prevents leaks. Eighty parts rubber melted with 20 parts beeswax is also good and is acid resisting.

Rubber Tube Connections. Coating the glass tube with a viscous solution f sealing wax, dissolved in alcohol, or etching it with hydrofluoric acid, on the ortion covered by the rubber will make a tight joint so that wiring the joint will ot be necessary.

Parallel Leveling Lines are placed behind the burette to enable more accurate eveling of the mercury columns.

(b) Nitrogen Oxides

Nitrogen tetroxide, N_2O_4, and nitrous acid, N_2O_3, can best be determined by absorption in standard permanganate (acidulated with sulphuric acid) according to p. 694.

Nitric oxide can be determined by passing the gases through soda lye, then by adding air to the collected volume, converting it to nitrogen tetroxide and determining it as above indicated.

Nitrous oxide is determined in the acid-free gases by explosion with hydrogen.

(c) **Oxygen** is usually determined by acid or ammoniacal cuprous chloride—phosphorus is also employed. The percentage of oxygen should not exceed six; a larger amount means that heat is being lost from the chambers by the exhaust gases. Knowing their temperature, the loss of heat can be calculated as with chimney gases.

V. MINE GASES [1]

The gases to be sought are those found in illuminating gas and for most purposes the procedure on p. 704 can be followed. For small quantities of methane the apparatus of Haldane, modified and described by Burrell and Seibert [2] should be used. This is practically an Orsat, using mercury as the confining liquid and with a compensating tube and grisoumeter for burning the methane.

For determination of **methane** alone, the apparatus of Shaw [3] may be recommended. This determines first the per cent of illuminating gas necessary to make an explosion of definite strength with ordinary air; when this has been done, mine air is used in place of the ordinary air and a smaller percentage of illuminating is required—smaller by the amount of combustible gas in the mine air. The strength of the explosion is measured by noting by the ear the force with which the plunger is driven out from the explosion cylinder against a bell.

In case this apparatus be not at hand, Brunck's [4] method can be employed. This consists in burning the methane in a 2-liter Erlenmeyer flask by means of an electrically heated platinum spiral. The flask carrying the spiral in the stopper is sunk inverted in a vessel of water and the current allowed to pass for half an hour, which is sufficient to burn the methane. It is then cooled and 25 cc. BaO_2H_2 (1 cc. = 1 cc. CO_2) added, time allowed for absorption of the carbon dioxide and the excess of BaO_2H_2 determined, p. 728, and the quantity of methane calculated.

Clowes and Redwood [5] have worked out a method for the detection of inflammable gas in air, employing the "flame cap." When an inflammable atmosphere is brought in contact with a candle or better a hydrogen flame, the gas burns, forming a "cap," like the colorless flame above the blue cone in a Bunsen burner: the length of the flame is a measure of the percentage of gas, and as little as 0.1% is visible using the hydrogen flame.

Carbon Monoxide. Besides combustible gases or "fire damp," it is sometimes necessary to get an idea of the amount of carbon monoxide ("white damp")

[1] See Technical Paper 14, Bureau of Mines, "Apparatus for Gas Analysis Laboratories at Coal Mines."

[2] Bull. 42, U. S. Bureau of Mines, 17, 42, 1913, also Technical Paper 39, 13.

[3] Berichte, 27, 692.

[4] O. Brunck, "Die Chem. Unters. d. Grubenwetter," 1908.

[5] "Detection and Estimation of Inflammable Gas and Vapor in the Air," 1896, also Clowes, J. Soc. Arts, 41, 307.

in the mine air after an explosion or in the "after damp"; chemical methods, p. 704, being too slow, use is made of the behavior of birds and mice when exposed to such an atmosphere. To this end they are carried in cages by the rescuing party and their behavior noticed. Canaries show distress in an atmosphere containing 0.15% of CO in five to twelve minutes, or with 0.20% in half this time: Mice are less sensitive,[1] and men may display distress when carbon monoxide is as little as 0.1%, whereas animals may be unaffected. In case either is overcome by the gas, resuscitation can be effected by bringing them out into the open air again. Repeated exposure of the gas would seem to be without influence.

VI. ELECTROLYTIC GASES

Gases from electrolytic chlorine, hydrogen and oxygen generators. The following are to be sought for:

(*a*) Chlorine, (*b*) oxygen, (*c*) carbon dioxide, (*d*) carbon monoxide, (*e*) hydrogen.

(a) Chlorine. Hempel[2] recommends measuring the gas quickly in his burette over water and then sucking in 5 cc. of 50% potassium iodide solution through the capillary and shaking; the diminution in volume gives the chlorine.

The other gases are determined in the usual way. As phosphorus cannot be used for pure oxygen, a specially prepared potassium pyrogallate, p. 735, is employed; cuprous chloride or ammoniacal cuprous carbonate in the absence of carbon monoxide is very satisfactory.

VII. ACETYLENE

Commercial acetylene may contain the following gases:

1. Oxygen;
2. Hydrogen;
3. Methane;
4. Nitrogen;
5. Sulphur-containing gases;
6. Phosphine.

Oxygen is estimated after the absorption of the acetylene itself in fuming sulphuric acid, in the usual way with potassium pyrogallate. Methane and hydrogen would be determined in this residue, after treatment with ammoniacal cuprous chloride to complete the removal of acetylene, by the ordinary explosion methods, p. 704. Nitrogen would be left as a residue.

Sulphur-containing gases. These are most likely organic sulphides, as hydrogen sulphide is probably absent, since the solution is strongly alkaline from which the acetylene escapes. They can be determined by combustion, as in illuminating gas, p. 716, and best be reported as "total sulphur."

Phosphine is also similarly estimated and the phosphoric acid determined in the usual way: the quantity of PH_3 rarely exceeds 0.05%. Acetylene can be purified by passing over bleaching powder, through acid cuprous chloride or chromic acid: The candle power is usually given as fifty per cubic foot, or 180–200, when burned at the rate of 5 cu.ft. per hour. The explosive limits are according to Clowes[3] 3 to 82%.

[1] Burrell, Seibert and Robertson, Bureau of Mines Technical Paper 62, 1914, "Relative Effects of Carbon Monoxide on Small Animals."

[2] "Gas-Analytische Methoden," 4th Ed., 1913, p. 278.

[3] Op. cit.

VIII. ATMOSPHERIC AIR

(*a*) Moisture; (*b*) Carbon dioxide; (*c*) Ozone; (*d*) Carbon monoxide; (*e*) Bacteria.

(a) Moisture [1] by chemical means, see p. 731. The amount of moisture can be determined by the sling psychrometer, or wet- and dry-bulb thermometer or by the hair hygrometer. The sling psychrometer is the most rapid and accurate—the wet- and dry-bulb thermometers are so arranged that they can be rapidly whirled for fifteen or twenty seconds, stopped and quickly read, the *wet* bulb first; this is repeated until closely agreeing readings are obtained. The humidity is determined in the usual manner from the meteorological tables.

The amount of moisture in the air is probably indirectly responsible for our sensations of comfort or discomfort, rather than the amount of carbon dioxide, as was formerly thought. This moisture controls the heat loss from the body, which loss must be normal—neither too high nor too low. The greater the humidity the less the evaporation, consequently the less the cooling.

For comfort, the higher the temperature the less should be the humidity; the following shows the relation between the two:

Temp., °F.	60	68 [2]	70	80	90
Relative humidity, per cent	67	40	49	31	16

(b) Carbon Dioxide. One of the most satisfactory methods is that of Hesse.[3] This consists in absorbing the carbon dioxide from a definite volume of air with standard barium hydroxide and determining its loss of strength.

FIG. 132.

The air is collected in heavy Erlenmeyer flasks of 100–500 or 1000 cc. capacity, or clear glass bottles; these are stoppered with doubly perforated rubber stoppers carrying glass plugs and the capacity of the flask or bottle noted to the depth of the stopper. A 10-cc. pipette and a 15-cc. glass-stoppered burette graduated in cc./10 with an 8-cm. tip, complete the outfit; a solution of 1.7 grams of barium hydroxide and chloride (20 : 1) in a liter of water, *B* Fig. 132, and of oxalic acid 5.6325 grams per liter (1 cc. = 1 cc. CO_2), with phenolphthalein 1 : 250, are required.

The bottles are filled with steam by exposure for three minutes and the vaselined stoppers inserted, or they may be filled with distilled water and opened in the place the air of which is to be examined.

In all this work, it should be remembered that the exhaled breath contains from 30 to 40 parts carbon dioxide per 10,000, consequently care should be taken not to contaminate the samples, nor should they be warmed with the hand.

[1] Benedict, "The Composition of the Atmosphere with Special Reference to its Oxygen Content," Carnegie Institution of Washington, 1912, Publication No. 166.
[2] For indoor work.
[3] Eulenberg's Vierteljahrschr. f. ger. Med. u. San. N. F., 31, 2.

The 10-cc. pipette is partly filled from the tube *A*, Fig. 132, by means of the rubber connector and sucking the liquid into the pipette: it is rinsed, filled and inserted through one of the holes in the rubber stopper of the bottle, the other plug being momentarily opened. The plugs are replaced and the bottles allowed to rest on their sides, with occasional rolling, for twenty minutes. Not more than one-fifth of the solution should be used up by the carbon dioxide present.

During this time, the barium hydroxide should be standardized; to this end a few drops of phenolphthalein and a quantity of the oxalic acid almost sufficient to neutralize the hydroxide should be run into a 100-cc. Erlenmeyer flask from the burette; this should be passed through the doubly perforated stopper; 10 cc. of the barium hydroxide solution are run into the flask as above described, and also the oxalic acid until a pink color appears.

Phenolphthalein is added to the bottles containing the samples, the oxalic acid burette inserted through the stopper and the excess of barium hydroxide titrated.

The barometric pressure and temperature in the laboratory are noted and the volume of the bottle less 10 cc. (BaO_2H_2) calculated to standard conditions; the difference in the titer of the barium hydroxide solution gives the volume of carbon dioxide in the bottle; this is calculated into parts per 10,000.

Other methods for this determination are more strictly gasometric, measuring the diminution in volume by absorption: Benedict [1] used Sonden's, and Anderson [2] recommends a shortened form of the Pettersson-Palmquist apparatus.

This may be described as an Orsat apparatus using mercury instead of water and with a 25-cc. burette the lower part of which is graduated to 0.0025 cc.; this is connected to a pipette of potassium hydroxide, a delicate manometer and compensating tube. The apparatus is delicate and rapid, but requires a skilled operator to manipulate it.

The amount of carbon dioxide in the outdoor air in the city is about 3.1 parts per 10,000, in the house, 3.7–3.9; with 6–7 parts in a room, the ventilation may be considered as excellent, with 10 parts as about the upper limit. In some theaters which were lighted by gas it approached 50 parts.

(c) **Ozone.** Probably most conveniently determined by Wurster's method, p. 697.

(d) **Carbon Monoxide.** The qualitative detection is most certainly effected by the blood test; to this end the gas is drawn through a solution of blood contained in a Wolff, Fig. 118, or similar absorption tube and examined for its absorption spectrum. The blood solution is made by mixing ox blood which has been defibrinated by whipping, with an equal quantity of a cold saturated solution of borax; this can be kept (as a side-shelf reagent) in the laboratory for months. This solution is diluted with 19 volumes of water, giving a solution of blood of 1 in 40 which is placed in the absorption tube. The air is drawn through it at a rate of 3 liters per hour, requiring 10 liters in some cases; the solution is put a thin flat-sided bottle and spectroscopically examined.

Pure diluted blood, Fig. 133, shows two dark absorption bands, spectrum 2, between the *D* and *E* line; these are welded into one broad band by reducing agents as NH_4SH, spectrum 4; blood which has absorbed carbon monoxide shows two

[1] Op. cit.
[2] J. Am. Chem. Soc., 35, 162, 1913.

broader bands in the same place, spectrum 3, which are unaffected by reducing agents. The quantitative determination depends upon the equation,

$$5CO+I_2O_5=5CO_2+I_2.$$

This has been studied by Kinnicutt and Sanford [1] and recently by Morgan and McWhorter[2] and by the writer. The process consists in sucking the air through the iodine pentoxide contained in a U-tube heated in cottonseed oil or glycerin bath to 150°, passing the iodine into potassium iodide solution and then absorbing the carbon dioxide in standard barium hydroxide. Both the iodine and barium hydroxide solutions are titrated. The last two investigators call particular attention to the ease with which iodine pentoxide at 150° is decomposed by organic matter, particularly stopcock grease; the pentoxide should be sealed into the U-tube, as glass stopcocks cannot be used. The writer can substantiate this statement, and would suggest further that the U-tube be chemically cleaned with cleaning solution ($Na_2Cr_2O_7+H_2SO_4$) before filling with I_2O_5, as well as the tubes through which the gas is sucked before reaching the U-tube; rubber connections should, if possible, be avoided, and the tubing should have been cleansed by warming with dilute soda lye and washing. The U-tube should be drawn down to the same size as the connecting glass tubing and the two butted closely together in the cleansed rubber connector.

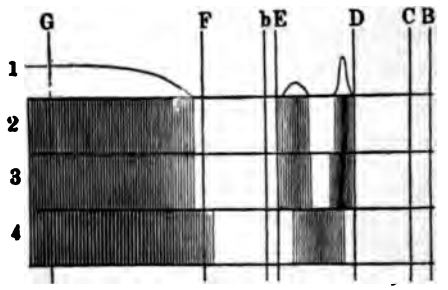


FIG. 133.

The iodine is titrated with N/1000 thiosulphate and every 2.27 mg. of iodine corresponds to 1 cc. of carbon monoxide under standard conditions; the carbon dioxide is absorbed in the hydroxide contained in a long test-tube 24×2.5 cm. and titrated with oxalic acid (1.1265 grams crystallized acid to 1 liter) using phenolphthalein; 5 cc. of the acid are equivalent to 1 cc. of carbon dioxide.

Haldane [3] states that as little as .01% of carbon monoxide can be determined colorimetrically by absorbing in diluted blood and comparing it with standard carmine solution; carbon monoxide turns the brownish yellow color of the blood to pink.

(e) **Bacteria.** See "Standard Methods for Bacterial Examination of Air." Am. J. Pub. Health, 6, No. 3, 1910.

[1] J. Am. Chem. Soc., **22**, 14, 1900.
[2] Ibid., **29**, 1589, 1907.
[3] Clowes, op. cit., 138.

DETERMINATION OF MOISTURE IN GASES

The gas to be tested is passed through a dehydrating agent such as phosphorus pentoxide, P_2O_5, alumina, Al_2O_3, or lime, CaO, contained in a weighed U-tube, Fig. 134. The following facts should be borne in mind in selecting the dehydrating agent: (*a*) It should not absorb the gas; (*b*) it should not react chemically with the gas. For example—lime or alumina could not be used for determining moisture in sulphur dioxide, nor could phosphorus pentoxide be used in determining moisture in ammonia. For the former, phosphorus pentoxide is best, and for the latter, lime. Alumina that has been carefully heated to 1400° is useful for determining moisture in neutral gases. It should be remembered that gases dried over calcium chloride will give up moisture to strong sulphuric acid, and these in turn will give up moisture to phosphorus pentoxide: Professor Morley has even determined the amount of moisture that is left after this latter treatment.

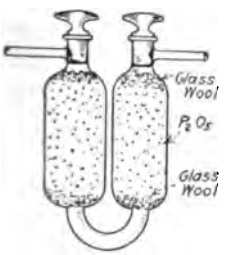


FIG. 134.

Procedure. The volume of the gases required for the test varies widely according to the percentage of moisture in the gas, 1000 cc. to 10,000 cc. are generally required. For minute amounts of moisture it may be necessary to lead the gas over the dehydrating agent for a given length of time, using a manometer or difference gauge, or a gas meter. The absorption tube is weighed before and after the test and the increase in weight taken as the moisture content of the gas.

Method of Determining Gasolene Vapor in Gaseous Mixtures.[1] Fig. 135 shows the apparatus for the gasolene-vapor determination. The bulb *a* contains phosphorus pentoxide for removing water vapor. If the latter were not removed it would also be retained at low temperatures and would subsequently exert pressure when measurement was being made of the pressure exerted by the gasolene vapor.

To start a determination the apparatus is connected to a vacuum pump and its air exhausted. The mixture of gasolene vapor and air is then introduced at atmospheric pressure, the barometer is read, and the two bulbs are immersed in liquid air contained in a Dewar flask. After about ten minutes, the air is removed from the apparatus with a vacuum pump. The stopcock on the apparatus is then closed, the liquid air in the Dewar flask removed, the gasolene allowed to vaporize, and its pressure read on the mercury manometer attached to the apparatus. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasolene vapor originally in the air.

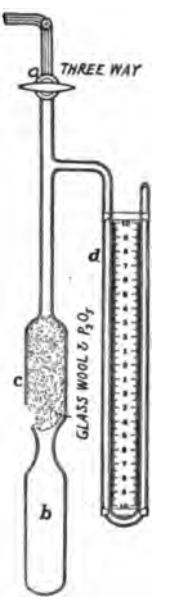


FIG. 135.

[1] U. S. Bureau of Mines, Technical Paper No. 115, Burrell and Boyd.

DETERMINATION OF NITROGEN BY THE NITROMETER[1]

The nitrometer, Fig. 136, consists of a gas-generating bulb fitted at the top with a two-way cock leading to a dissolving cup and a gas-exit tube, and which has at the bottom a connection for a rubber tube leading to a leveling tube, the whole being filled with mercury to a level just below the upper cock; a cylindrical glass measuring tube graduated from 0–100 cc. connected to a leveling tube through

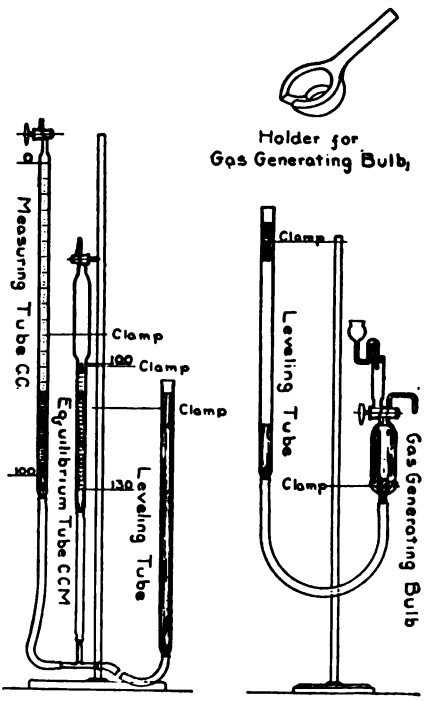


FIG. 136.

a T-tube leading to an equilibrium tube. The latter is shaped like an inverted 100-cc. pipette graduated downward below the bulb from 100–130 cc. The whole system is filled with mercury so that the measuring tube may be completely discharged by raising the leveling tube.

Adjusting the Equilibrium Tube. The volume of 100 cc. of dry air at 0° C. and 760 mm. under the temperature and barometric conditions prevailing at the time is calculated, 3 drops of 98% sulphuric acid are drawn into the tube and the level of the mercury fixed in accordance with the calculation. The cock of the tube is then closed and sealed with melted paraffin. The volume in this tube may be confirmed at any time by opening the measuring tube and adjusting the leveling tube so that the level is the same in the three tubes. The volume of gas in the equilibrium tube is then read and compared with the calculated volume

[1] Joyce and La Tourette, J. Ind. and Eng. Chem. **5**, 1017, 1913.

at the time, a correction in the subsequent gas readings in the measuring tube being made accordingly.

Nitrogen in Potassium Nitrate. Approximately 0.4 gram potassium nitrate is placed in a weighing tube, dried two hours at 110° C., desiccated twenty-four hours over sulphuric acid and weighed exactly by difference into the cup of the gas-generating bulb. This is dissolved in 9 cc. 95% sulphuric acid, added through a siphon thistle tube, entering the top of the dissolving cup through a tight-fitting rubber stopper. When the salt is dissolved it is drawn into the gas-generating bulb and followed by two washings 1.5 cc. each of 95% acid. The bulb is then shaken with a motion normal to its long dimension until the volume of gas determined by a rough paper scale pasted on the leveling tube becomes constant, this operation taking from three to five minutes.

The gas is passed into the measuring tube, and after standing five minutes the leveling and measuring tubes are so adjusted that the level in the equilibrium tube reads 100 cc. and is the same as the level in the measuring tube. The reading of the latter is then taken. As the temperature and barometric conditions, in so far as they affect the measured volume of the gas, are automatically compensated by the equilibrium tube, and as the gas is washed with sulphuric acid and is, therefore, dry, the percentage of nitrogen may be calculated directly, correcting only for the calibration of the equilibrium and measuring tubes. Seventeen determinations made when the room temperature ranged from 20–28° gave 13.71% nitrogen, the theoretical being 13.84%.

The nitrometer gives reliable results within 0.02% in nitrate nitrogen, using 0.4–0.5 gram sample. It is not available for the determination of nitrogen in celluloid or other substances containing carbon ring compounds which appear to prevent the complete liberation of nitric oxide in the presence of sulphuric acid and mercury.

Besides the corrections for calibration and standardization of the nitrometer in accordance with temperature and barometer, the gas readings should be corrected for solubility of nitric oxide, which diminishes when the temperature goes above 28° C., and the formation of other gases by the breaking up of the cellulose molecule which increases.

The following table gives the algebraic sum of these two corrections for temperatures ranging from 20° to 35° C.

Temp.	Cc.	Temp.	Cc.
20.0–27.5	+0.90	30.0	−0.14
28.0	+0.74	30.5	−0.70
29.0	+0.34	31.0–35.0	−0.94

REAGENTS AND TABLES

The reagents used in gas analysis, particularly in the absorption apparatus, are comparatively few and easily prepared.

Hydrochloric Acid, Sp. gr. 1.10. Dilute "muriatic acid" with an equal volume of water. In addition to its use for preparing cuprous chloride, it finds employment in neutralizing the caustic solutions which are unavoidably more or less spilled during their use.

Fuming Sulphuric Acid. Saturate "Nordhausen oil of vitriol" with sulphuric anhydride. Ordinary sulphuric acid may be used instead of the Nordhausen; in this case about an equal weight of sulphuric anhydride will be necessary. *Absorption capacity,* 1 cc. absorbs 8 cc. of ethene (ethylene).

Acid Cuprous Chloride. The directions given in the various text-books being troublesome to execute, the following method, which is simpler, has been found to give equally good results: Cover the bottom of a two-liter bottle with a layer of copper oxide or "scale" $\frac{3}{8}$ in. deep, place in the bottle a number of pieces of rather stout copper wire reaching *from top to bottom,* sufficient to make a bundle an inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp.gr. The bottle is occasionally shaken, and when the solution is colorless, or nearly so, it is poured into the half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp.gr.).

By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

The absorption capacity of the reagent per cc. is, according to Winkler, 15 cc. CO; according to Hempel 4 cc. The author's experience with Orsat's apparatus gave 1 cc.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to keep out the air, which turns the solution brown and weakens it.

Ammoniacal Cuprous Chloride. The acid cuprous chloride is treated with ammonia until a faint odor of ammonia is perceptible; copper wire should be kept in it similarly to the acid solution. This alkaline solution has the advantage that it can be used when traces of hydrochloric acid vapors might be harmful to the subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

Absorption capacity, 1 cc. absorbs 1 cc. CO.

Cuprous chloride is at best a poor reagent for the absorption of carbonic oxide; to obtain the greatest accuracy where the reagent has been much used, the gas should be passed into a fresh pipette for final absorption, and the operation continued until two consecutive readings agree exactly. The compound formed by the absorption—possibly Cu_2COCl_2—is very unstable, as carbonic oxide may be freed from the solution by boiling or placing it *in vacuo;* even if it be shaken up with air, the gas is given off, as shown by the increase in volume and subsequent diminution when shaken with fresh cuprous chloride.

Hydrogen. A simple and effective hydrogen generator can be made by joining two 6-in. calcium chloride jars by their tubulatures. Pure zinc is filled

in as far as the constriction in one, and the mouth closed with a rubber stopper carrying a capillary tube and a pinchcock. The other jar is filled with sulphuric acid 1 : 5 which has been boiled and cooled out of excess of air. The mouth of this jar is closed with a rubber stopper carrying one of the rubber bags used on the simple pipettes.

Mercury. The mercury used in gas analysis should be of sufficient purity as not to "drag a tail" when poured out from a clean vessel. It may perhaps be most conveniently cleaned, except from gold and silver, by the method of J. M. Crafts, which consists in drawing a moderate stream of air through the mercury contained in a tube about 3 ft. long and 1¼ ins. internal diameter. The tube is supported in a mercury-tight V-shaped trough, of size sufficient to contain the metal if the tube breaks, one end being about 3 ins. higher than the other. Forty-eight hours' passage of air is sufficient to purify any ordinary amalgam. The mercury may very well be kept in a large separatory funnel under a layer of strong sulphuric acid.

Or Meyer's method [1] may be used. A separatory funnel is used to hold the mercury. The delivery tube of the funnel is slightly narrowed 0.5 cm. from the lower end. Over this side is bound with twine a piece of rather closely woven muslin. The mercury is allowed to flow through the cloth into a solution of mercury nitrate contained in a tall cylinder, with stopcock at the lower end. The tip of the funnel with the muslin dips under the surface of the cleaning solution. The purified mercury is drained off from the bottom of the cylinder. It can also be purified except from traces of zinc by distillation.

Palladous Chloride. Five grams palladium wire are dissolved in a mixture of 30 cc. hydrochloric and 2 cc. nitric acid, this evaporated just to dryness on a water bath, redissolved in 5 cc. hydrochloric acid and 25 cc. water, and warmed until solution is complete. It is diluted to 750 cc. and contains about 1% of palladous chloride. It will absorb about two-thirds of its volume of hydrogen.

Phosphorus. Use the ordinary white phosphorus cast in sticks of a size suitable to pass through the opening of the tubulated pipette.

Potassium Hydrate. (*a*) For carbon dioxide determination, 500 grams of the commercial hydrate are dissolved in 1 liter of water.

Absorption capacity. One cc. absorbs 40 cc. CO_2.

(*b*) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydrate are dissolved in 100 cc. of water.

Potassium Pyrogallate. Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 grams of the solid acid upon a paper, pour it into a funnel inserted in the reagent bottle, and pour upon it 100 cc. of potassium hydrate (*a*) or (*b*). The acid dissolves at once, and the solution is ready for use.

If the percentage of oxygen in the mixture does not exceed 28, solution (*a*) may be used;[2] if this amount be exceeded, (*b*) must be employed. Otherwise carbonic oxide may be given off even to the extent of 6%.

Attention is called to the fact that the use of potassium hydrate purified by alcohol has given rise to erroneous results.

Absorption capacity. One cc. absorbs 2 cc. O.

[1] J. H. Hilderbrand, J. Am. Chem. Soc., **31**, 934.
[2] Clowes, Jour. Soc Chem. Industry, **15**, 170.

Sodium Hydrate. Dissolve the commercial hydr
of water. This may be employed in all cases wher
hydrate is used. The chief advantage in its use
pyrogallate is, however, a trifle slower in action tha
sium salt.

TABLE 1

TABLE SHOWING THE TENSION OF AQUEOUS VAPOR AND A
CONTAINED IN A CUBIC METER OF AIR W

From 5° to 30° C.

Temp.	Tension, mm.	Grams.	Temp.	Tension, mm.	Grams.
5	6.5	6.8	14	11.9	12.0
6	7.0	7.3	15	12.7	12.8
7	7.5	7.7	16	13.5	13.6
8	8.0	8.1	17	14.4	14.5
9	8.5	8.8	18	15.4	15.1
10	9.1	9.4	19	16.3	16.2
11	9.8	10.0	20	17.4	17.2
12	10.4	10.6	21	18.5	18.2
13	11.1	11.3	22	19.7	19.3

Moisture in the Air.[1] Twenty tests made on differen
17th to November 10th, 1916, at a period agreeing closely
conditions, gave results varying from 0.1510 gram to (
standard cubic foot. The average of the results was 0.246
of air. Omitting three rainy days of this period the ave
laboratory (75° F.) was found to be 0.2141 gram per cubi

It is an interesting fact that at 75° F., 52 per cent sul
standard) is in equilibrium with air containing 0.2137 g
according to an average of results by W. W. Scott and a
on tension of aqueous vapor in mixtures of sulphuric acid

TABLE 2

SPECIFIC HEATS OF GASES AT CONSTA

Air	
Carbon dioxide	
Carbonic oxide	
Hydrogen	
"Illuminants"	
Methane	
Nitrogen	
Oxygen	
Aqueous vapor	

The "volumetric" specific heat is the quantity of h
perature of 1 cu.ft. of gas from 32° F. to 33° F.

[1] Communicated by W. W. Scott.
[2] H. L. Payne, Jour. Anal. and Applied (
[3] Ethylene.

TABLE 3

CALORIFIC POWER OF VARIOUS GASES[1] IN BRITISH THERMAL UNITS PER CUBIC FOOT

Name.	Symbol.	60° F. Initial.	32° F. Initial. 32° F. Final.	Ignition Point °F.
Hydrogen	H_2	326.2	345.4	1085[4]
Carbonic oxide	CO	323.5	341.2	1200[4]
Methane	CH_4	1009.2	1065.0	1230
Illuminants[2]	....	.....	2000.0	.....
Ethane	C_2H_6	1764.4	1861.0	1140
Propane	C_3H_8	2521	2657.0	1015
Butane	C_4H_{10}	3274	3441.0	.....
Pentane	C_5H_{12}	.....	4255.0	.....
Hexane[3]	C_6H_{14}	.....	5017.0	1400
Ethylene	C_2H_4	1588	1674.0	1010[4]
Propylene	C_3H_6	2347.2	2509.0	940
Benzene	C_6H_6	3807.4	4012.0	.....
Acetylene	C_2H_2	1476.7	1477.0	788[4]

TABLE 4

1 cubic inch = 16.39 cc.
1 cubic foot = 28.315 liters
1 cubic meter = 35.31 cu.ft.

1 calorie = 3.969 B.t.u.
1 pound = 453.59 grams

[1] H. L. Payne, loc. cit.

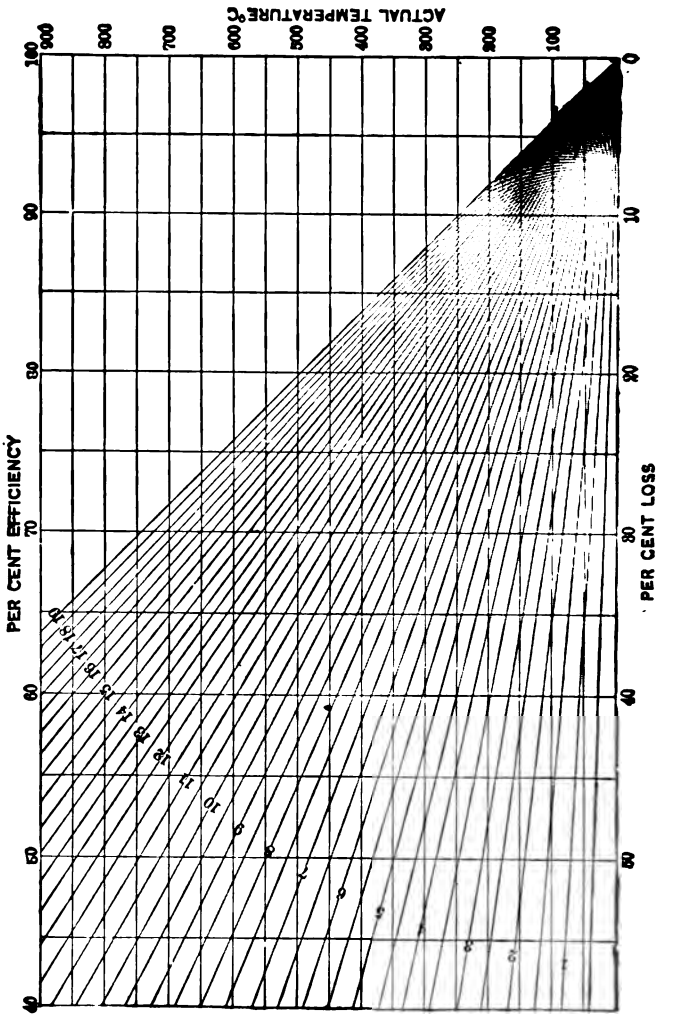
[2] Where the "illuminants" are derived chiefly from the decomposition of mineral oil.

[3] The chief constituent of the "gasolene" used in the gas machines for *carbureting* air.

[4] Dixon and Coward, Proc. Chem. Soc., **26**, 67.

TABLE 5

BUNTE'S CHART



FURNACE METHODS OF ASSAYING FOR GOLD AND SILVER

WALLACE G. DERBY [1]

THE SAMPLE

The unit of weight in assaying all classes of material except gold and silver bullion is the assay ton, 29166.6 milligrams; the same number of milligrams as there are ounces troy in a ton of 2000 avoirdupois pounds. If one A.T. of material be taken for assay, the number of milligrams gold or silver obtained represents ounces per ton and is so designated in reports. In the assay of all classes of bullion except copper and lead, results are calculated to and reported in terms of parts per thousand. Synonymous with parts per thousand are the terms fine, fineness, parts or degrees fineness.

The sample received by the assayer should not only be representative of the material undergoing valuation or investigation, but should be in such a state that the operator can, without extraordinary manipulation or precaution, weigh out portions which are exactly like the sample. As a general rule no sample of pulverized material should have a fineness of less than 80 mesh. With increase of value or decrease of proportion of the constituent of the material which carries the values, the fineness should be increased to 100, 120 or even 200 mesh, unless the attempt to obtain such homogeneity is accompanied by introduction of so much matter worn from the grinding mill or plate, or by change of weight due to oxidation of some constituent, as to decrease rather than increase the representative character of the assay portions. The sample of material which is composed of particles very unlike in value and so dissimilar in such physical properties as size, weight, magnetism, hardness, etc., which make separation practicable, should be presented to the assayer in fractions representative of the components. A convenient rule (an algebraical contraction of the arithmetical operation), for calculating the assay of the whole from the assays of the components which for convenience will be called coarse and fine, may be stated as follows: Multiply the difference of the assays of the coarse and fine by the decimal fraction representing the percentage of fine in the material and, if the assay of the fine is greater than that of the coarse, add the product to the assay of the coarse; but if the assay of the fine is less than that of the coarse, subtract the product from the assay of the coarse. To a known weight of some sorts of material, during the process of sampling, reagents are added to neutralize and dry acid substances or water is added to prevent dusting of light and fine substances. To calculate the assay to original basis; multiply by 1 plus the decimal fraction representing the per cent increase of weight. Occasionally organic matter is removed by combustion, barren matter by magnetism or other methods, and very commonly moisture by drying. To calculate to original basis; multiply the assay by 1 minus the decimal representing

[1] Research Chemist, Nichols Copper Company, New York.

the per cent decrease in weight of the sample. Samples of material which have the property of changing weight with atmospheric conditions, should be kept in tightly stoppered bottles. The assay of such material is best made on the portion of the sample used in the determination of moisture. The distribution of values in solid copper or lead bullion is never uniform. Unhomogeneity tends to increase with quantity of impurity and with decrease in the rate of cooling from the molten state. The sample of copper bullion should be composed of drill shavings from every part of the piece which is practicable to attack with a ½ or ¾-in. twist drill in such a manner that the particles from each part shall have the same proportionate weight in the sample as the part is of the whole piece. This principle is applied to the sampling of the multiplicity of pieces composing a lot of copper. In lot sampling a single hole is drilled through the top or bottom of each piece of a definite fraction of the total pieces in a lot. The position of the drill is changed with successive pieces so that it will attack in turn the center of all the equal-sized squares composing a pattern or " templet " which will exactly cover one-quarter, one-half or the whole of the top of the average piece. The squares should be as small as is practicable to drill, about 1 in. It is considered the best practice to drill one-half of the holes in blister copper top to bottom, the remainder bottom to top, also when drilling according to a quarter or half templet, to change hand side with every other round of the templet. All the shavings are ground to pass a 20-mesh screen by a drug mill with hard steel grinding plates. The sample of lead bullion, like that of copper, should be composed of the due proportion of particles from every part of the single piece. The end is attained by using for sample the sawdust from complete cuts with a circular saw at equal and definite intervals along the length of the piece. In lot sampling a single cut is made in a definite fraction of the total number of pieces in the lot. The position of the cut is changed with successive pieces, so that it will pass through the longer axis of each of the equal-sized rectangles composing the pattern or templet which will exactly cover one-half or the whole of the top of the average piece of the lot. To make accurate sampling possible, it is evident that the pieces composing a lot of either copper or lead bullion should be symmetrical in form and alike in size, shape and grade. At regular intervals during the process of pouring lead bullion into moulds, samples may be taken in the form of shot, but most satisfactorily in the form of slugs or bullets, each weighing close to the amount customarily taken for assay (½ or 1 A.T.) and composed of the entire contents of the ladle used for dipping. All classes of gold or silver bullion and Doré metal are most accurately sampled by taking just after thorough stirring and immediately before pouring several dip samples of about 3 grams each with graphite ladles. The metal is allowed to cool in the ladle or may be granulated by pouring into warm water. When the lot of bullion is large, samples are taken at definite and regular intervals throughout the ladling period. Except in the case of bullion of a high degree of fineness, sampling by drilling or by cutting chips from the corners of bars is not as satisfactory as the methods described.

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FURNACE OPERATIONS

The several furnace operations employed in assaying have for their object:

(1) To eliminate in part or entirely from the material undergoing assay, organic matter and such elements as sulphur, arsenic, antimony or selenium when present in sufficient quantity to cause excessive reducing effect in the crucible fusion, interference with decomposition, mechanical or other loss by either method of fusion. When the operation does not cause greater loss of values than its avoidance by skillful fluxing, elimination by combustion or roasting is practiced.

(2) To produce such conditions that the greatest quantity of gold or silver in the material subjected to assay can through their affinity be concentrated in molten lead. This is brought about by two methods.

a. ***By the crucible method,*** the material is mixed with no larger quantity of reagents called fluxes than will form, with all its basic or acid constituents at a moderate temperature, compounds of the greatest degree of fluidity. Simultaneously with the progress of the fusion, lead, generated from lead oxide by an added reducing agent or by the property of the material itself, percolating the fluid, collects the precious metals and also some portion of such other constituents which combine or alloy with lead under the conditions of the fusion.

b. ***By the scorification method,*** the material, in contact with a relatively large mass of lead in shallow dishes called scorifiers, is decomposed and fluxed chiefly by lead oxide, the greater part of which is formed by the action of atmosphere on the molten lead. When the proportion of volume of material or flux is not too great, the fluid slag collects about the sides of the scorifier leaving the surface of the lead exposed to oxidation, which may be allowed to progress until the increasing proportion of slag covers the lead. The precious metals and a portion of such other alloyable metals in the charge are collected by contact with the molten lead. During scorification, elements forming readily volatile oxides such as sulphur, arsenic, and selenium are in process of elimination in the form of vapor, while the elements—iron, manganese, antimony, zinc, cobalt, tin, nickel, cadmium, copper, bismuth, selenium and tellurium—when taken up in one form or another by lead during the fusion period of the operation, are carried into the slag at rates which depend in part upon the property to oxidize characteristic of the element, in part upon the concentration of the element in the lead, and in part on the properties of the associated elements.

(3) To procure with the least loss of gold and silver their alloy with lead in the form of a lead button which can be cleaned of adherent slag and is of suitable size (10 to 20 grams) and sufficiently free of base elements to make possible by the operation of cupellation, the production without greater loss than if the base elements were absent, of a silver-gold bead of normal purity. Size of button is controlled in scorification by observation, in crucible fusion by incorporation in the charge of the proper amount (which is determined by trial or experience with similar material), of oxidizing reagents when the material has an excessive reducing property; of reducing reagent when the material has not an excessive reducing, neutral or oxidizing property. Purity of button is obtained by the scorification method by repetition of the operation, with addition each time of lead until the shade of color of the glazed portion of the scorifier

or appearance or properties of the lead button indicate to the experienced operator the presence of impurity in less quantity than will prevent faultless cupellation. By each method the amount of metallic impurity in the button can be diminished by increasing the proportion of litharge in the charge. With increase of quantity of base element, its restraint from the button becomes impracticable by the crucible method; purification of the button by process of scorification is therefore resorted to in all cases except when bismuth or copper associated with selenium or tellurium are present. These elements are best eliminated by a wet method.

(4) To separate from lead which may contain a small amount of other metals an alloy of the precious metals in weighable form and in a definite state of purity, 996–998 fine.

Separation by cupellation is effected by taking advantage of the non-susceptibility of gold or silver to oxidation, the heat of formation of lead and other metallic oxides, the fluid character of lead oxide at the temperature of its formation, the solubility of a limited amount of metallic oxides, and the sparing solubility of gold and silver in fluid lead oxide, the perviousness to fluid lead oxide of bone ash of about the same temperature and the imperviousness of the same material to molten gold, silver or lead.

Consequent to the furnace operations, except when it is known that gold is absent, is the wet process of separating in weighable form and in a very definite state of purity (997 to 998 fine) gold from silver in the bead obtained by cupellation.

The process of parting depends upon the fact that when the proportion of gold in the alloy is not too great, silver can be dissolved almost completely by hot dilute nitric acid with but small corrosive effect upon the gold.

Preliminary to furnace operations, it is advantageous in the assay of some classes of material to subject the sample to treatment by nitric or sulphuric acid with the object of eliminating all or a greater part of the base elements and of concentrating the precious metals into a mass of small volume. The procedure is practicable when the character of the material is such that the residue resulting from the treatment does not interfere with filtration and when gold is not dissolved or liberated in so fine a state that it cannot be retained by a filter. Dissolved silver is precipitated as chloride, bromide, sulphide or metal. Procedures which introduce the feature of preliminary acid treatment are called combination methods.

Silver and gold are retained in the slag from both the crucible and scorification method of fusion. When the product of assay of slag is added to the result of the primary operation, the assay is said to be carried out with slag correction.

Silver and gold are carried into the cupel to a greater extent per unit of lead eliminated than into slag by scorification of lead containing the same concentration of precious elements. When the silver or gold so retained is determined, either by subjecting the cupel to assay processes or by check cupellation of a known and similar quantity of the precious metals under the same conditions, and the result obtained added to the product of the primary operation, the assay is said to be carried out with correction for cupellation loss.

Corrected assay is the term applied to the result which includes a correction for silver and gold lost into the slag and cupel. It is not customary to take account of the fineness of the silver or gold mass, or of gold dissolved in the operation of parting.

Determination of gold, even when silver is known to be absent, is much more accurately made by weighing the product of the operation of parting its alloy with a suitable proportion of silver than the gold bead resulting from cupellation. Loss of gold in cupellation tends to decrease with increase of the ratio of silver present.

The precautions taken in furnace operations to prevent abnormal silver loss should be observed as a rule in the assay for gold only.

Determination of silver is performed by weighing the bead resulting from cupellation and subtracting from this weight the amount of gold obtained from the operation of parting.

Influence of quantity of sample taken for a single determination can be derived relatively from Chart Fig. 138, which shows that the per cent of loss in the operation of assaying blister copper by the sulphuric acid combination method decreases as the proportion of precious metals in the charge increases. Cupellation has a larger influence ordinarily in this direction than the operation of fusion. The fact is of consequence in the assay of material for purchase and sale, for it is evident that unless the valuation be made on the basis of corrected assay, or a complete understanding by all parties interested exists as to the details of the methods of assaying employed, con-

versy may arise because of the consistently higher value which will be put on the terial by the assayer who uses the larger assay portion in his practice. For instance, in the valuation of blister copper containing 50 ozs. silver per ton, should sayer A representing one party be in the habit of using 2 A.T. assay portions, his

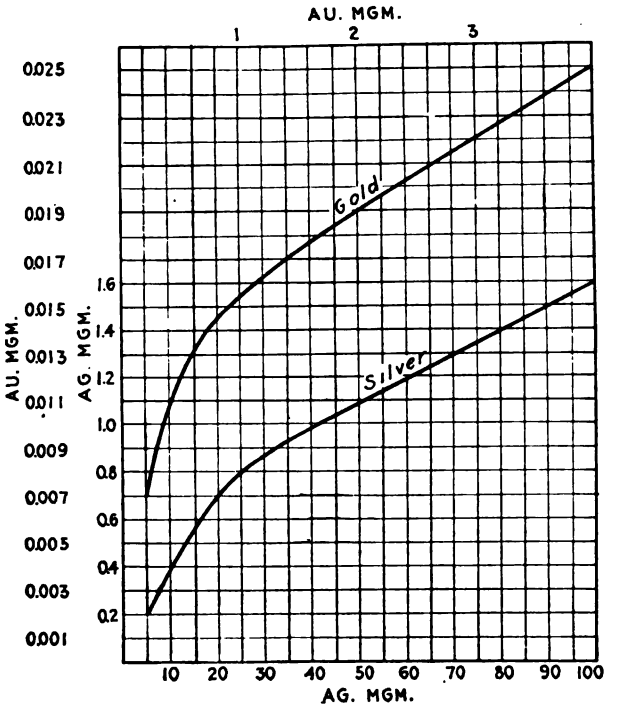

FIG. 138.

valuation of the lot will be on the basis of $\frac{98.4}{2}$ or 49.2 ozs. per ton, while B, who uses the same method as A but customarily carries out his operations on 1 A.T. portions, will report 48.82 ozs. per ton, or a result about 0.8% lower than A.

ROASTING INCINERATION

In laboratories performing many assays by combination methods, incineration of filters is accomplished by placing the scorifiers on trays which fit the shelves of an oven like that of a gas stove. The furnace muffle is, however, commonly employed for the purpose. Loss of particles of the charge is prevented by covering the folded paper with granulated or sheet lead and burning slowly at a low temperature. Sprinkling the inside of filters with litharge hastens combustion. Carbonaceous matter in material like reverberatory or blast-furnace flue-dust is removed by combustion in a muffle. The same matter in zinc retort residue cannot be removed by incineration without considerable loss of silver. Roasting of pyritic material is carried out on the portions weighed out for assay in scorifiers if the sulphur has little other metallic base than iron; in large roast-

CRUCIBLE METHOD OF FUSION

This operation may be performed in a wind or crucible furnace, but best in a muffle. If the furnace is to be used for crucible fusion alone, the muffle need have a single draft hole only in the top. Although the operation is less subject to irregularities when carried out in a muffle tight to the products of combustion, satisfactory fusions are made in gas, or liquid fuel furnaces from which the muffles have been removed. The most convenient shape and size of crucible to muffle fusions are the 5, 10, 20 or 30 grams, Colorado form. The 10 and sometimes the 5-gram crucible is used for fusion of filter paper residues from combination methods. The 20-gram is used for ½ A.T., the 30-gram crucible for 1 A.T. ore portions. The cinder from roasted fine pyrite mixed with water makes a good paint for marking crucibles or scorifiers.

Litharge, melting at 888° C., is a basic flux, an oxidizing and therefore desulphurizing agent. It is the source of metallic lead for collecting the precious metals. With borax it forms a very fluid glass. Its functions are expressed by the following reactions:

$2PbO+SiO_2=2PbO\cdot SiO_2$

$PbO+Na_2CO_3+SO_2=Na_2SO_4+Pb+CO_2$

$ZnS+3PbO=ZnO+3Pb+SO_2$

$Ag_2S+2PbO=2PbAg+SO_2$

$PbS+2PbO=3Pb+SO_2$

$C+2PbO=2Pb+CO_2$

$Sb_2S_3+9PbO=9Pb+Sb_2O_3+3SO_2$

$Sb_2S_3+6PbO=Pb_6Sb_2+3SO_2$

$2Cu_2S+7PbO=2CuO+Cu_2O+7Pb+2SO_2$

$Sb_2+3PbO=Sb_2O_3+3Pb$

Lead oxide dissolves metallic oxides. The following table [1] shows the extent of this property.

Per one part of.....	Cu_2O	CuO	ZnO	Fe_3O_4	Fe_2O_3	MnO	SnO_2
Parts of litharge required..	1.5	1.8	8	4	10	10	13
Per one part of.....	SbO_2	As_2O_3	As_2O_5				
Parts of litharge required..	5	0.8	1				

Sb_2O_3 is very soluble in litharge.

Five hundred grams of lead oxide should contain no gold, less than 0.0005 gram silver, and no bismuth. According to the amount of litharge used, such silver as it contains should be deducted from the weight of the bead in the assay of material in which the normal range of assay error is measured in hundredths rather than tenths of an ounce.

Floated silica, analyzing over 95% SiO_2, and so fine that 90% will pass a 200-mesh screen is an excellent and easily obtainable form of the reagent. Silica in the form of powdered glass, averaging 70% to 75% SiO_2, is an acid flux. Its addition to a basic charge should be limited to the formation of a slag which is less than a bisilicate.

Borax glass, $Na_2O\cdot 2B_2O_3$, melting at 878° C., may be considered an acid or basic flux. As an acid flux, it combines with the metallic oxides to form a very fluid slag. As a basic flux it may be employed in the assay of acid ores, with a value nearly equal in weight to that of litharge.

Soduim carbonate, anhydrous, melting at 849° C., sodium bicarbonate which commences to decompose at 270° C., and potassium carbonate, anhydrous, melting at 909° C. are basic fluxes. Sodium bicarbonate in its decomposition and reaction with silica liberates three times as much gas per unit of base as the normal carbonate.

[1] Hofman, "Metallurgy of Lead."

By some assayers this property is considered a virtue on account of the stirring-up action on the charge. In the use of bicarbonate the danger of spoiled assays due to boiling over and mechanical loss through dusting is great. Potassium carbonate in the form of refined pearl ash, is of value on account of the fluidity of the potash silicates. It is deliquescent and when dried and in form for use as a flux must be kept out of contact with moist atmosphere. Sodium carbonate is used in the form of refined soda ash. A mixture of equal weights of soda and pearl ash is a good form of flux. Besides its function as a base for silica in the charge, the alkali flux operates to increase the amount of lead reduced from lead oxide by a sulphide.

$$4Na_2CO_3+15PbO+2FeS_2=Fe_2O_3+4CO_2+15Pb+4Na_2SO_4.$$

By the addition of 3.1 parts of Na_2CO_3, 23 parts of lead are reduced by 1 part of sulphur. In the absence of the alkali, the reaction would be $FeS_2+5PbO=FeO+2SO_2+5Pb$, according to which only 16 parts of lead are reduced by 1 part of sulphur. The reaction of the alkali flux with lead sulphide is like the following:

$$7PbS+4Na_2CO_3=4Pb+Na_2SO_4+3(PbS\cdot Na_2S)+4CO_2.$$

Reducing Agents. In case the charge is not of a reducing nature, one of the reagents in the table is added in quantity which experience with the same type of material, knowledge of its composition or preliminary trial indicates is sufficient to reduce a suitable amount of lead to collect the precious metals.

The following table shows the approximate reducing power of the reagents in common use:

Grams lead reduced	by 1 gram of reagent.
22 –30	Charcoal
6 –11	Argol (crude tartar)
4.5– 6.5	Cream of tartar
10 –15	Wheat flour
11.5–14.5	Sugar
22 –25	Coal or coke
11.5–13	Corn or laundry starch
11 –12	Pyrite (FeS_2)

To assist distribution or contact with the largest number of particles of litharge it is of advantage to use an agent which is in a very fine state of division and of low reducing power per unit of volume. Argol is a popular reagent. The writer uses starch. A carbonaceous reducing agent reacts with silicate of lead with a sluggishness which increases with the silicate degree above the monosilicate, but the presence of other bases, especially the alkaline, operates to make the reaction more complete.

$$2PbO\cdot SiO_2+2Na_2O+C=2Na_2O\cdot SiO_2+CO_2+2Pb.$$

Iron in the form of twenty-penny nails or ¼-in. iron wire can be used as a reducing agent and desulphurizing agent in the assay of material which contains little or no base impurities, such as copper, tin, antimony. Its functions are expressed by the following reactions:

$$Fe+PbS=FeS+Pb$$

$$Fe+FeS_2=2FeS$$

$$PbO+Fe=FeO+Pb$$

$$2PbO\cdot SiO_2+2Fe=2FeO\cdot SiO_2+2Pb$$

$$PbS\cdot Na_2S+Fe=FeS+Na_2S+Pb$$

Potassium nitrate, saltpeter, melting when pure at 337° C., or sodium nitrate, nitre, melting when pure at 316° C., are oxidizing and therefore desulphurizing agents. Sodium nitrate is deliquescent. Either salt should be dried, very finely pulverized and kept in a stoppered bottle.

The nitrates decompose on heating,

$$2KNO_3=2KNO_2+O_2;$$

and at a higher temperature,

$$2KNO_3 = K_2O + 2NO + O.$$

Their behavior in fusions is illustrated by the following reactions:

$$4FeS_2 + 10KNO_3 = 4FeO + 5K_2SO_4 + 3SO_2 + 5N_2;$$
$$4ZnS + 6KNO_3 = 4ZnO + 3K_2SO_4 + SO_2 + 3N_2.$$

When an alkaline base is present the reaction is

$$2FeS_2 + 6KNO_3 + Na_2CO_3 = Fe_2O_3 + 3K_2SO_4 + Na_2SO_4 + CO_2 + 3N_2.$$

Nitrates act on metallic lead

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2.$$

Salt, melting at 804° C., is used in a thin layer as a cover over the top of the charge in the crucible. It is very fluid when melted and having a low gravity, floats on the fusion. Its function is to prevent the charge from boiling over or spattering. When moist it decrepitates and on that account may cause loss of particles of the charge. It should be dried before use.

Fluxing. All substances from which precious metals are to be effectively collected by crucible fusion must necessarily be in a fine state of division, and mainly composed of compounds which may be classified as acid or basic. Acid is the characteristic applied to material which contains silica, free or combined with too little base to form a readily fusible substance. Basic is the term applied to metallic or earthy oxides, or compounds which may be brought to the state of oxide in the process of fusion. In this form they are capable of forming salts with silica. These salts are defined by the ratio to each other of oxygen in the acid and base. By the metallurgical classification their names are as follows:

Formula.	Name.	Oxygen Ratio Base to Acid.	Example.
$4RO \cdot SiO_2$	Subsilicate	2 to 1	$4PbO \cdot SiO_2$
$2RO \cdot SiO_2$	Monosilicate	1 to 1	$2Al_2O_3 \cdot 3SiO_2$
$RO \cdot SiO_2$	Bisilicate	1 to 2	$CaO \cdot SiO_2$
$4RO \cdot 3SiO_2$	Sesquisilicate	2 to 3	$4MgO \cdot 3SiO_2$
$2RO \cdot 3SiO_2$	Trisilicate	1 to 3	$2PbO \cdot 3SiO_2$

The silicates of Na_2O, K_2O and PbO are readily, MnO, FeO, and Cu_2O, less; and MgO, CaO, and Al_2O_3 difficultly fusible. To make the refractory silicates fusible and fluid at moderate temperatures, the proportion of their bases should be less in the fusion than the bases of the readily fusible silicates. Advantage is also taken of the fact that the multibasic silicates are more fusible generally than the single of the same degree.

A rule governing the fluxing of a crucible charge is very definitely stated by Fulton,[1] "The most desirable constitution for an assay slag, in general, is that of a monosilicate or sesquisilicate, sometimes, but more rarely, a bisilicate. If the ore is basic, a bisilicate slag may be approached, if acid, a monosilicate or even a subsilicate."

[1] "Fire Assaying," 2d ed., 69.

TO FORM A MONOSILICATE THE REQUIREMENT

	Na_2O	K_2O	PbO	MnO	FeO
Per unit of base, silica required.....	0.486	0.320	0.135	0.425	0.419
Per unit of silica, base required.....	2.06	3.12	7.40	2.35	2.37

	Al_2O_3	CuO	ZnO	CaO	MgO
Per unit of base, silica required.....	0.886	0.379	0.371	0.359	0.748
Per unit of silica, base required.....	1.13	2.64	2.70	2.64	1.34

A crucible fusion should not be fluxed by borax or litharge alone. No more borax should be used than is required to combine with bases and silica in the proportion illustrated by the equations:

$$2(Na_2O,\ 2B_2O_3)+SiO_2=2Na_2O\cdot SiO_2+4B_2O_3,$$

$$B_2O_3+3FeO=3FeO\cdot B_2O_3.$$

As a flux for silica, 6.7 parts borax will take the place and can be substituted for 7.4 parts litharge, 3.5 parts Na_2CO_3, 5.4 parts $NaHCO_3$ or 4.6 parts K_2CO_3. As a flux for bases, assumption of 3RO, B_2O_3 works out well in practice.

	FeO	CaO	MgO	ZnO	PbO
Required of borax per unit of base.....	0.937	1.20	1.67	0.807	0.302

"In the fusion of a mixture containing silica, various bases and borax glass, that silicate borate having the lowest formation point will form and then as the temperature rises, absorbs either silica, base or both, as these are in excess of the ratio required to form the lowest formation point compound. If the temperature does not rise high enough to cause this absorption, the excess of silica or base or both will remain in suspension in the formed silicate borate, practically in an unaltered condition." [1]

Materials intended for crucible assay are characterized according to their behavior toward lead or lead oxide as oxidizing, reducing or neutral. The oxidizing constituents of an ore are practically limited to Fe_2O_3, Fe_3O_4, MnO_2 and CuO. Substances containing unoxidized sulphur, antimony, arsenic or carbon, on fusion with litharge produce metallic lead. When an arsenide is present with iron, nickel or cobalt a brittle fusible substance called speiss will be found in the crucible above the lead. Also when iron is present and the quantity of litharge has not been sufficient to oxidize all the sulphur, a sulphide compound of iron and lead called matte will be found above the layer of speiss. When the silver content of the ore is small, the ore can be roasted in the manner already described. The roasted ore then as a rule becomes oxidizing in its behavior. To obtain a lead button of suitable size, knowledge of the oxidizing power

[2] Fulton, "Fire Assaying," 2d ed., 64.

of the ore is obtained from experience or by trial assay. Having once determined the reducing power of the reducing reagent, for instance starch, by fusion of its intimate mixture with the charge without the ore, ½ A.T. of the ore is roasted and then fused with 50 grams litharge, 2 grams starch, accurately weighed out, 10 grams soda ash and 8 grams silica. A thin layer of borax or salt covers the charge in the crucible. If the reducing power of the 2 grams of starch is known to be 22 grams and only 15 grams of lead are produced by fusion of the ore, the oxidizing power of the ore is equivalent to $\frac{2(22-15)}{22}=0.636$ gram starch per half A.T. 2.636 grams of starch therefore should be used to obtain a 22-gram button.

Since roasting causes inappreciable loss as a rule only in the case of material of low silver value, oxidation by addition of nitre to the fusion is the more generally practiced. Theoretically the oxidizing value of 1 gram of KNO_3 is 2.39 grams of lead according to the reaction

$$7Pb+6KNO_3=7PbO+3K_2O+6N+8O.$$

The reducing power of $\frac{1}{10}$ A.T. of the ore is determined by trial fusion with 60 grams of litharge, 5 grams silica, 7 grams Na_2CO_3 and borax cover. Assume the product is a button weighing 16 grams. A fusion may then be made with the same charge but with 1 gram of nitre added. Assuming the product of the nitre fusion to be 12 grams, then the oxidizing power per gram of nitre is 16−12 or 4 grams under the conditions of the fusion. If the assay is to be made on a ½ A.T. portion and a 25-gram button is desired, then $(16\times5)-25=55$, and $\frac{55}{4}=13.75$ grams nitre to be added. When sulphur is oxidized by nitre, care should be taken that sufficient Na_2CO_3 is in the charge to carry out the reaction:

$$6KNO_3+Na_2CO_3+2FeS_2=Fe_2O_3+3K_2SO_4+Na_2SO_4+6N+CO_2.$$

Theoretically the quantity of Na_2CO_3 required is 0.84 of the sulphur present or 0.175 of the nitre used.

The oxidizing power per gram of nitre, when sufficient Na_2CO_3 is present, ranges from the equivalent of 4.7 to 5.6 grams lead in a litharge soda charge and 4.0 to 4.2 grams in a charge containing so much silica that little of the alkaline base is left to form a sulphate.

In practice, the requirement of quick results does not always permit of trial assays for determination of oxidizing or reducing power. Estimation of the reducing value of sulphide ores can be made by experience gained by observation of the proportion of heavier sulphide to gangue on vanning a definite weight of a sample in a shovel or porcelain spot plate.

Instead of weighing out each of the fluxes at the time of dressing a crucible, it is the practice to make up for each type of ore a stock mixture of all or part of the reagents adapted to its assay, and to measure out the flux with a graduate.

Oxidizing and reducing reagents, when not incorporated in a stock flux, are weighed out carefully.

The following are examples, the first from Fulton [1] "Reducing flux designed to give a 22-gram button with a neutral charge:

[1] "Fire Assaying," 150; Hawley, Eng. and Min. Jo., 89, 1122; 90, 647

		Grams per ½ A.T.
PbO,	15 parts	60
Na_2CO_3,	4 "	16
Borax,	2 "	8
Flour,	0.44 "	1.75

" A scoopful of flux weighing 84 grams is used per ½ A.T.

" Non-reducing flux to be used in connection with nitre for sulphide ores which will give a button larger than 22 grams.

		Grams per ½ A.T.
PbO,	15 parts	60
Na_2CO_3,	3.5 "	14
Borax,	2.5 "	10
Silica,	0.5 "	2
Nitre		As required

"When sulphide ores are assayed which do not contain sufficient sulphides for a 22-gram button, the reducing and non-reducing fluxes are mixed in such proportion as to obtain the desired result. Ore 3.64 grams; non-reducing flux 50 grams. This is run in a 10-gram crucible. This charge will give a lead button weighing as much as the nitre necessary to oxidize all the sulphides in a 0.5 A.T. portion of the ore. Place the lead button obtained in one scale pan of the pulp scale and from the hook above the other suspend by fine wire a weight so that the wire amounts to 6 grams. Then add nitre to the pan having the 6-gram weight until the scale is in balance. The amount of nitre is the proper quantity necessary to reduce a 22-gram button with the ore and the non-reducing flux is 0.5 A.T. be taken for assay."

The following stock fluxes are used by a well-known New York firm of assayers.

No. 1 flux for free acid ores without much sulphides or reducing agents.

	Lbs.	%	Grams per A.T.
Soda ash	6½	22.8	31.9
Pearl ash	2½	8.8	12.3
Silica	2½	8.8	12.3
Borax glass	4	14.0	19.6
Litharge	12½	44.0	61.6
Argol	½	1.7	2.4

Use 140 grams per A.T. of pulp. Argol may be increased as the individual charge requires.

No. 2 flux for basic ores without much sulphate or other reducing agents.

	Lbs.	%	Grams per A.T.
Soda ash	5	17.2	24.1
Pearl ash	2½	18.6	12.0
Silica	4½	15.5	21.7
Borax glass	4	13.8	19.3
Litharge	12½	43.1	60.3
Argol	½	1.0	2.4

Use 140 grams per A.T. of material. Argol may be increased in the individual charge.

No. 3 flux for heavy copper sulphides containing but little silicious matter.

	Lbs.	%	Per ½ A.T.
Litharge	40	84.2	252.6
Soda ash	3½	7.4	22.2
Silica	4	8.4	25.2

Use 200 to 300 grams flux per ½ A.T. of pulp, less for lighter, more for heavier sulphides. Reduce the very large lead button weighing 90 to 120 lbs. by scorification. Varying mixtures of No. 1 and No. 3 are employed for sulphides ores carrying considerable silica. High grade litharge free of bismuth is essential. Soda ash is the ordinary high test commercial variety. All ingredients should be finely powdered and thoroughly mixed by repeatedly passing the flux through a coarse screen or by turning a mixing cylinder.

By the following method [1] a large excess of litharge is supplied to dissolve or prevent reduction of metal oxides. Because the silver loss into the slag tends to increase with excess of litharge and volume of the slag, the method is applicable to material which contains copper or other metals in such quantity that repeated scorification is required to complete their removal when a less proportion of litharge is used.

The type of charge per crucible usually is:

Ore	0.25–0.5 A.T.
PbO	8–10 "
Na_2CO_3	12 grams
SiO_2	10 "

Nitre or reducing agent in quantity sufficient to obtain a 20-gram button.

Proportion of PbO to assay portion is increased or diminished according to experience with the kind and quantity of metal which is to be kept from the button.

The iron nail method is applicable to sulphur-bearing ores which do not contain much copper or other impurities alloyable with lead.

Since iron reduces PbO, the amount of litharge in the charge is limited to 25 to 30 grams. The slag should be below the monosilicate and the charge should be sufficiently high in soda to make certain the completion of the reaction $7PbO+FeS_2+2Na_2CO_3=7Pb+2Na_2SO_4+FeO+2CO_2$, else matte will be formed. When arsenic is present the temperature should not be above 1050° C.,[2] else speiss may form. A typical charge is:

	Grams.
Ore	0.5
Na_2CO_3	20
PbO	30
SiO_2	2
Borax	8

Iron equivalent to three twenty-penny nails is introduced in such a form and

[1] Perkins, Trans. Am. Inst. Min. Eng., **31**, 913.
[2] Fulton, "Fire Assaying," 122.

manner that just before pouring, the portion above the charge can be seized firmly by suitable tongs, freed of adherent lead by knocking against the side of the crucible and then withdrawn.

Ores containing a great deal of silica and little of metallic oxides may be fused with a charge similar to the following:

Ore	½ A.T.
PbO	30 grams
Na_2CO_3	30 "

Reducing agent sufficient to produce a 20-gram button.

In the assay of ores containing selenium or tellurium, these metals must be practically eliminated from the lead before cupellation. Both have a great affinity for lead and copper and unless the fluxes are well proportioned and the fusion skillfully carried out, the product will be a brittle button which cannot be detached from the slag. Tellurium reacts with litharge at moderate temperature. 700 to 900° C.[1] before silicates of lead are formed, according to the reaction $2PbO+Te=Pb_2O+TeO$. Partial reversion of the reaction takes place during the formation of silicates. When litharge has reacted sufficiently to form silicates there is no longer any oxidizing effect on tellurium.[2] In the assay of gold telluride ores it is the best practice to make a crucible fusion with a large quantity of litharge and to cupel directly or after scorification. The passage of tellurium into the slag is more complete in the case of a basic than an acid slag. The following are type charges:[3]

	Hillebrand and Allen's charge for Cripple Creek Ore.	Silicious Ore with Slight Reducing Power.	Cripple Creek Ore Containing 15–25% Al_2O_3.
Flour	1 A.T.	0.5 A.T.	0.5 A.T.
Ore	6 A.T.	100 grams	45.5 grams
Litharge		30 "	9 "
Na_2CO_3		.....	10.5 "
K_2CO_3	10 grams	6 "	8.5 "
Borax	when required	1.1 "	
Charcoal	when required	.....	1.5 "
$NaHCO_3$	1 A.T.		

Litharge cover. Salt should not be used.

The fusion of 1 and 2 should be carried out at a low temperature 950–1000° C., for 45 minutes, and finished by quickly raising the temperature, for a short period. Fusion of 3, which is not an excess litharge charge, is conducted at a temperature above the melting-point of gold, 1063° C., for the same length of time.

Silicious furnace by-products from the smelting of electrolytic slime from a copper refinery may contain selenium and tellurium in much larger percentage than is usual in ores. Especially when associated with copper, uniform results are most certainly obtained by a crucible fusion with a large excess of litharge of the largest assay portion which will produce a button which can be detached from the slag. Copper, selenium and tellurium are removed by wet treatment described on page 772.

In the assay of zinc-bearing material, loss of the precious metals through entrainment may be great if in any part of the process fume of zinc oxide is evolved.

[1] Smith, Trans. Inst. Min. and Met., 17, 473.
[2] E. A. Smith, "Assay of the Precious Metals," 227.
[3] Fulton, Fire Assaying, 131–136.

On that account, whenever it is practicable material containing metallic zinc should be subjected to acid treatment preliminary to the furnace operation. Loss into the slag may occur, through incomplete decomposition on account of the refractoriness of zinc silicate or because of the low solubility of zinc oxide in litharge.

The following is a type charge for ½ A.T. of ore containing a high percentage of zinc sulphide.

	Grams.
Litharge	100–200
Soda	10– 15
Silica	5– 10
Borax	5

Nitre sufficient to produce a 20 to 25-gram button. Borax glass cover.

The final temperature of the fusion should be about 1100° C.

When antimony in quantity is present, the crucible charge should contain a larger proportion of either litharge or soda. The following are type charges for ½ A.T. of an ore containing a high percentage of sulphide of antimony.

	No. 1.* Grams.	No. 2.† Grams.
Litharge	150	50
Soda	10	35
Borax	6	10
Silica	10	

* Fulton, Manual of Fire Assaying, 146.
† E. A. Smith, Assaying of Precious Metals, 222.

Nitre sufficient to produce a 25-gram button.

Salt used as cover.

As a rule a little antimony will contaminate the button and should be removed by a five or ten-minute scorification with about 10 grams of litharge.

In the assay of tin ores or concentrates, consideration must be given to the low solubility of tin oxide in litharge. The following are type charges:

	No. 1.	No. 2.*
Ore	¼ A.T.	½ A.T.
Litharge	150 grams	35 grams
Soda	10 "	25 "
Borax	5 "	5 "

* Bannister, Trans. Inst. Min. and Met., **15**, 513.

Reducing agent sufficient to produce a 20-gram button.

By method No. 2 it has been found necessary to clean the slag when the ore contains over 1 oz. of gold. The slag is therefore pulverized and fused with a mixture of 20 grams litharge, 6 grams soda and sufficient reducing agent to produce a 20-gram button.

Nickel and cobalt silver ores always contain arsenic, usually antimony and sometimes as much as 10% of silver, of which a portion may be in the form of large particles of very pure metal. Handy[1] describes the following: The charge

[1] Eighth Int. Cong. Appl. Chem., 1912, Sect. IIIA.

for the crucible, 0.2 oz. pulp, 12 grams K_2CO_3, 12 grams Na_2CO_3, 6 grams borax, 60 grams litharge and 1 gram of flour. "These are mixed by rolling in a rubber cloth, transferred to a crucible, covered with borax glass and heated to a medium red heat for twenty minutes. The door of the gas-fired muffle is then shut and the crucible heated to a bright yellow for thirty minutes."

The following are efficient charges employed in the process of corrected assay. Because calcium phosphate is not decomposed by the fusion, it is necessary in the assay of the cupel that it should be very finely powdered—no coarser than 120 mesh.

	Slag.	Saturated Portion of Cupel.
Material	100 parts	100 parts
Litharge	25 "	100 "
Soda	10 "	40 "
Borax	5 "	75 "

Reducing agent, sufficient to produce a 20-gram button, is added and thoroughly mixed with each material while it is being pulverized. Salt is used for cover. The fusion of the cupel powder should be finished at a high temperature. The button from slag containing copper, antimony, tin, nickel or cobalt may require scorification with addition of lead before it becomes suitable for cupellation. Purification of the lead button may also be accomplished by melting it in a crucible or scorifier with litharge sufficient to cover it and a pinch of silica or borax. When the slag is fluid, the crucible is given a rotary motion, either within or without the furnace. This treatment is continued at intervals for five to ten minutes before pouring.

In the conduct of the crucible method, it is of extreme consequence when the material is neutral or oxidizing in its action that there should be very intimate mixture of the assay portion with the reducing agent and with litharge. When reducing in action, the finely pulverized nitre should be thoroughly mixed with the assay portion.

The operation of mixing is conveniently accomplished by use of a 10- or 12-in. porcelain mortar with glazed inner surface, or by rolling on a 30-in. square piece of smooth rubber cloth. Soda should be well mixed with the charge but not necessarily so intimately as to lose its identity. Silica and borax may be roughly mixed. The use of a cover of salt or borax is of advantage in all fusions in which much gas, CO_2, CO, SO_2 or H_2O is liberated.

Salt is not recommended as a cover of charges high in silver or gold. If the crucible is heated too slowly, the greater part of the lead may be reduced and run to the bottom of the crucible before complete decomposition of that constituent of the ore which carries the precious metal has taken place. When heated too speedily, that compound of base and borax with the silica of the ore which has the lowest formation point will sink to the bottom of the charge, leaving a pasty, unbalanced charge above. Moreover, evolution of the gases may not only cause mechanical loss, but on account of their expulsion before the material undergoing assay is entirely decomposed, the effect of their stirring action is lost.

Fusion. As a rule it is good practice to place crucible into a muffle which is at about 850 to 900° C. The introduction of the crucibles cool the furnace to about 550 to 600° C. Without altering the rate of introduction of heat to the fur-

nace, the flow of heat to the crucible charge continues until at the end of twenty-five to thirty minutes evolution of gas ceases. The fire is then urged for ten to fifteen minutes until a temperature of about 1100° is reached, when the crucibles are withdrawn from the muffle and poured into a dry, clean, shallow-bottomed or conical mould. The slag should be very fluid and free of any evidence of undecomposed ore. If the slag is pasty, the necessity of modifying the flux is indicated. If the nature of the flux is such that the crucible is very much corroded, it is good practice to pour off most of the slag and permit the lead, covered with slag, to solidify in the crucible.

SCORIFICATION

Scorification is most efficiently carried out in a muffle sealed from the products of combustion and having a rectangular opening in the back nearly the

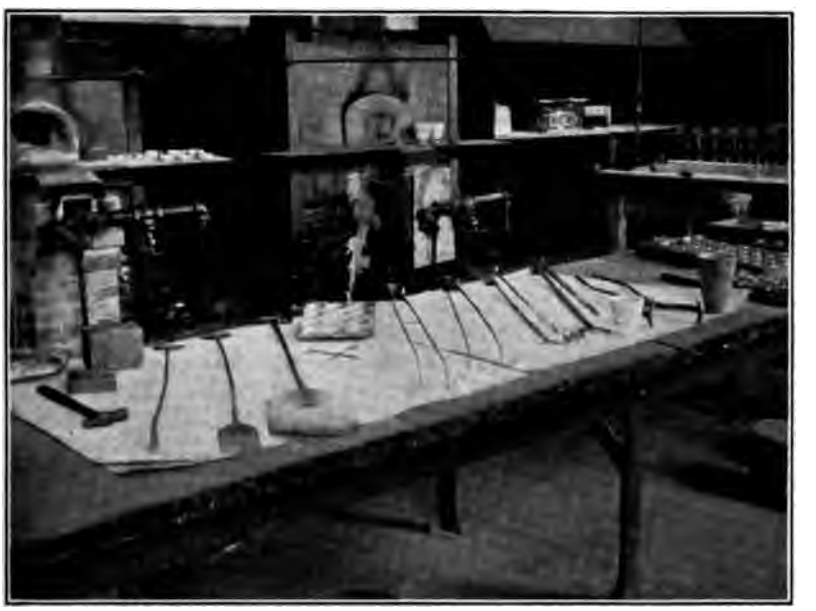

FIG. 140.

full width of the muffle and about on the level with the top of the scorifiers. The opening should be connected with a flue pipe fitted close to the furnace with an easily controlled damper. The draft head from a chimney 10 ft. in height is effective. The life of a muffle is prolonged by a layer of bone ash or silica sand over its floor and by adequate support of the entire bottom. Mixture of 1 part fire-clay with 3–4 parts silica sand serves well to lute the muffle to the furnace. Alundum cement is better for filling cracks in the muffle.

The best form of scorifier is the Bartlett shape. The nearly flat bottom of this type gives room for a larger accumulation of slag about the molten lead than a rounder bottomed scorifier of the same diameter. The sizes of scorifier

commonly employed are the 2, 2½, and 3 inch. For the fusion of ore or other material, when it is of advantage to use as large as possible charge of either assay portion or of lead, the 3-in. size is employed. For the fusion of filter paper residue, from which a moderate quantity of impurity such as copper, silica or iron, is to be removed, the 2½-in. size is adapted. The 2-in. size is used for filter paper residue of small volume, which contains so little impurity objectionable in the process of cupellation that only short scorification is required.

Moisture and especially salts absorbed by a scorifier will cause spurting of the lead during scorification. For this reason, scorifiers should be kept dry, and those intended for reception of moist substances should be first glazed with lead borate or silicate, or lined with a single sheet of lead foil.

The reagents used are limited to granulated test lead, sheet lead, borax glass, silica and litharge.

Granulated lead is commonly of such degree of fineness that 50% or more will pass a 60-mesh screen. The sheet lead most generally used weighs 1.5 to 1.75 grams per square inch. The amount of gold in 500 grams of lead should be and generally is unweighable. While the lead should contain no bismuth or silver, it too frequently carries as much as 0.005% of bismuth, and 0.0002% of silver. The silver content should be known and correction on account of it should be applied to results from material, the assay error of which is measured in hundredths rather than tenths of a milligram.

Borax glass alone is always used as a flux for silicious material. Silica alone is used in all rescorifications. A mixture of equal parts of borax and silica is used to flux basic charges.

Litharge mixed with the assay portion of any refractory material increases the rate of its decomposition.

The scorification method is especially applicable to the fusion of filter paper residue in combination methods of assaying, to gold or silver ores and to copper or lead refinery by-products which are so rich that 0.1 or 0.05 A.T. constitutes the test portion, and to the assay for gold in material in which gold is less and silver more accurately determined by combination methods, such as some high copper ores, furnace and refinery products. Scorification is employed to purify lead, either as sample or the product of the crucible fusion, of impurities which are objectionable in the process of cupellation. The scorification method of fusion can be applied to low-grade silver-and gold-bearing silicious material, but usually gives the lower result and requires more furnace space and attention of the operator than the crucible method. Of such material, it is the practice to make fusions of portions of 0.1 to 0.25 A.T. each, and on the single button or on combinations of the buttons, with or without addition of more lead, second, third or even fourth scorifications are made until a button of suitable purity and size is obtained which represents 0.5 or 1 A.T.

The size of charge and detail of method of manipulation to produce the button for cupellation in the assay of any single type of material depends upon the size and shape of muffle and scorifiers, and the quality of draft. For instance, with a muffle of 6 ins. or more of inside height, having a draft hole and flue area 10–12% of the area of cross-section of the inside of the muffle, it is possible to scorify at the back of the muffle without pouring off the slag 60 grams of lead in a 3-in. Bartlett-shaped scorifier of American manufacture, to a 15- to 20-gram button. While a 30- to 50-gram button will be the product of the scorification in a muffle of such low form that it is difficult to keep the surface of the slag cool, or in one unequipped to maintain a rapid rate of oxidation, or in a scorifier of

smaller size, or of the same diameter but of a shape which does not provide amply for accumulation of slag before the lead becomes covered.

The ratio of weight of assay portion to that of lead is limited by the specific volume of the material and by the characteristic solubility of the actual and potential bases and of silica by lead oxide.

The volume of the assay portion, except in the case of material which is wholly metallic, when mixed intimately with one-half of the charge of granulated lead, should be no greater than can be covered by the remainder of the charge, else a part of the assay portion may adhere to the side of the scorifier out of contact with the slag. The assay portion should be no greater than will be completely dissolved by flux and lead oxide during the first few minutes of the scorification with formation of much less volume of slag than will cover the molten lead, else particles of the assay portion may float to the side of the scorifier and will remain undecomposed because out of reach of the portion of the slag which is in active circulation. In the dry or " all-fire " assay of metals alloyable with lead, the proportion of the assay portion and the concentration of metals during the first or succeeding scorifications should be no greater than will allow of the ready solution of the oxides by lead oxide at the rate of its formation, else a solid scum of oxide may form over the lead, preventing further scorification; or the oxides may aggregate in pasty lumps which tend to retain values in the slag. Oxidation of the metals progresses in approximately the following order: iron, zinc, tin, arsenic, antimony, lead, cobalt, nickel, copper, bismuth, selenium and tellurium. It is sometimes impracticable to eliminate completely the last three elements from lead by process of scorification. Because of their effect on the bead obtained by cupellation, whenever consistent assays for silver are sought, they are best removed from the lead button by the method described on page 772. The presence of selenium unassociated with other colored oxides is indicated by a ruby-colored slag. Tellurium gives a dark stain over the bottom of the scorifier. Antimony is indicated by orange-yellow patches on the scorifier. Iron gives a reddish brown, cobalt a brilliant blue and nickel a light-brown color to the scorifier glaze. Copper is oxidized comparatively slowly by scorification and the progress of its elimination by repeated scorification is indicated by the shade of the green glaze on the scorifier. When the concentration of copper in the lead has been reduced to such an extent that the lighter shades of green are obtained, the experienced operator is able to judge by observation of the size of button and the depth of color of the scorifier how much lead is required in the charge for final scorification, and when the button is sufficiently free of copper to permit of cupellation. A 10-gram button suitable for cupellation should be from a scorifier which is no darker than a very light apple green; a 20-gram button may be from a somewhat deeply shaded scorifier. If too little flux, silica or borax is supplied to a scorification, the scorifier is apt to be so deeply corroded or pitted that lead will be retained, while if too much borax is added the slag will be so viscous as to prevent aggregation of the particles of lead.

Silica, if unmixed with the assay portion, may be added in moderate excess, but may give some trouble in pouring. It is not uncommon practice to make a poor batch of scorifiers usable for assay of basic material by tamping a layer of fine silica over the bottom of each dish. In the assay of basic or acid ores or furnace products, as quick fusion as possible should be made. The scorifiers are put into a muffle having a temperature between 1050° and 1100° C. and the door and damper are closed tightly until (within ten minutes) the

scorifiers are of the same temperature as the muffle. The door and damper are then opened and by regulation of the means of supplying heat, the scorification is conducted at as low temperature as is practicable, until experience indicates that the buttons are of the size desired. The temperature of the muffle is then raised by closing the door and urging the fire for several minutes, when the contents of the scorifiers are poured into shallow iron moulds. Pouring with certainty of not shotting the slag is made easy of accomplishment by use of a mould no deeper than will just hold the contents of the scorifier, tongs with a very short prong on the pouring side and a motion which introduces the greater part of the slag a distinct interval before the lead is allowed to flow without much drop into the middle of the mould. When the scorifier remains in the furnace for some time after the lead is submerged, the slag becomes pasty and tends to cause more or less loss of lead in pouring. Thickening of the slag through entrance of the constituents of the scorifier is also brought about even before the lead is closed over, when the scorification is carried out at too a high a temperature or under any condition which causes corrosion of the scorifier at a greater rate than the production of the quantity of lead oxide requisite to keep the slag fluid.

Rescorifications to purify or concentrate the buttons are made at as low temperature as possible. Scorification of filter paper residues containing little else than gold and a silver precipitate may be commenced at a low temperature, but such as contain sulphur in any form should be started at a high temperature, else a portion of the sulphur oxidizing to SO_4 forms with the base of the borax flux, sodium sulphate, which may cover the lead and prevent oxidation of the sulphur which has combined to form lead sulphide.

Placing powdered charcoal on the surface of the slag before raising the temperature to pour, is not an effective method of cleaning the slag or of making an assay with slag correction. Because it introduces a factor likely to be personal and not wholly under control, the practice is not good in the appraising assay of commercial material.

Type Schemes. The following are illustrative of the details of manipulation of the scorification method of fusion, purification of lead and preparation of the button for cupellation.

Cobalt, Nickel Silver Ore. For each test of an ore containing over 2000 to 4000 oz. per ton, a button representing $\frac{1}{4}$ A.T. is cupelled. For each test of an ore containing 1000 to 2000 oz. per ton, a button representing $\frac{1}{2}$ A.T. is cupelled. For each test of an ore containing less than 1000 oz. a button representing 1 A.T. is cupelled. For each test of the metallic scale, which is quite pure silver, a button representing $\frac{1}{10}$ A.T. is cupelled. Of the 2000 oz. ore, $\frac{1}{4}$ A.T. is weighed out and mixed on smooth paper or rubber cloth with 90 grams of finely granulated lead and 9 grams powdered borax glass. The charge is distributed between three 3-in. scorifiers and each portion is covered with 30 grams of lead. Scorification, commencing at a high temperature, is continued at a low temperature until 15- to 20-gram buttons are produced. The buttons are combined in a single 3-in. scorifier, and rescorified to production of a 15- to 20-gram button which represents $\frac{1}{4}$ A.T. Of the 1000 to 2000 oz. ore, $\frac{1}{2}$ A.T. is weighed out, mixed with 150 grams of lead and 15 grams powdered borax, and distributed among five 3-in. scorifiers. The content of each scorifier is covered with 20 grams of lead. After scorification to production of 10- to 15-gram buttons, all the buttons are combined in a single 3-in. scorifier and scorified to production of a 15- to 20-gram button. The 1000 oz. or less ore is treated in exactly the same manner as the 1000- to 2000-oz. grade with the exception that two lots of $\frac{1}{2}$ A.T. each are weighed out and distributed among two groups of five scorifiers each. The two buttons resulting from the second scorification are combined in a $2\frac{1}{2}$-in. scorifier and by a third scorification a single button

representing 1 A.T. is produced. Of the metallic scale $\frac{1}{10}$ A.T. is weighed out, placed in a 2½-in. scorifier with 30 grams of lead and scorified to production of a 15- to 20-gram button. It is customary in the case of nickel silver ore to report results on the basis of assay with both slag and cupel correction, therefore all the slag in the production of each bead for cupellation should be collected, ground finely and the whole, or a convenient aliquot, assayed by the method described on page 754.

Assay of Blister Copper for Gold. For each test of ½ A.T., five lots of the sample of $\frac{1}{10}$ A.T. each are placed in three scorifiers and covered with 60 grams lead and 2 to 3 grams of the borax silica flux. Scorification is continued to production of 20- to 25-gram buttons. Sufficient lead is added to each button to make the total charge 60 grams and each $\frac{1}{10}$ A.T. portion is rescorified until about 20 grams of lead remain in each scorifier. From each scorifier the slag is decanted on the shelf in front of the muffle. Without removal from the furnace, all the buttons are combined by pouring into a single hot, fresh scorifier. Scorification is continued until about 25 grams of lead remains, the temperature is then raised, the slag decanted and the metal poured into a fresh scorifier holding 40 grams of molten lead. Scorification is continued to production of a 15- to 20-gram button. From the shade of the scorifier and size of the button, the operator judges how much lead is required to be added to procure from the fourth scorification a button suitable for cupellation. Throughout the operation the copper should not be allowed to become so concentrated or the temperature so low that lead will liquate from the copper.

Whenever muffle space is more valuable than time saved by combining portions of the assay by pouring from one scorifier into another in the furnace, it is the better practice to pour the portions into moulds and combine the slag-free buttons.

Copper Matte for Gold. For each test of ½ A.T., three lots of $\frac{1}{6}$ A.T. each are placed on a layer of 30 grams of lead in three 3-in. scorifiers. The charge in each scorifier is covered with 30 grams of lead and 5 grams of borax-silica flux. The scorifiers are placed in a very hot muffle which is opened only after the scorifiers are of the same temperature. The scorification is continued at as low temperature as possible, until 15 to 20 grams of lead remains in each scorifier. The heat is then raised for three to five minutes before pouring.

If the matte is very low in copper the buttons may be combined and rescorified to suitable size for cupellation. If the matte contains 10% to 20% copper, the product of the second scorification is rescorified with sufficient lead to make the total charge, according to the judgment of the operator, 30 to 60 grams.

If the matte contains 20% to 40% copper, each button of the first scorification is put into a fresh 3-in. scorifier and sufficient lead added to make the charge up to 30 to 60 grams. The product of the 15- to 20-gram buttons of the second rescorification are combined and reduced to cupellation size.

If the matte contains 40% to 60% copper, the product of the third scorification is scorified a fourth time with addition of sufficient lead to make the total charge 30 to 60 grams.

If the matte contains more than 60% of copper, each lot of $\frac{1}{6}$ A.T. is rescorified twice with addition each time of sufficient lead to make the total charge in each scorifier 40 to 60 grams. The resulting buttons are combined into a single charge for a fourth and final scorification to a 15- to 20-gram button. The details of the scheme are the same for the assay for silver or gold in ore of similar copper content, except that several grams of borax are mixed with the charge to flux the initial fusion.

Tin Concentrates for Gold and Silver. For each test, 1 A.T. mixed with 200-grams test lead, 100 grams litharge and 30 grams borax on smooth paper, rubber or oil cloth, is distributed among ten 3-in. scorifiers and each charge covered with 30 grams lead. Scorification, commenced at a high temperature, is continued low until the lead is covered over. The resulting buttons are pounded free of adherent slag, distributed among 2 or 3 scorifiers and rescorified. When the lead has been reduced in each to 15 to 20 grams, the charges may be poured and the resulting buttons combined and scorified to a final button; or the slag may be poured off and all the lead poured into a single scorifier. This method is also adapted to the assay of highly silicious material.

The methods described may be modified in the following details: For purpose of accounting, factory, mine or mill control, or by agreement between buyer and seller, the button to be cupelled may represent a smaller portion; because it is difficult to pick from the cupel and clean very small silver beads, cupellation of a portion repre-

senting two or more A.T. may be undertaken. When scorifiers are of uncertain quality, it is the better practice to weigh out the portion designed for each scorifier and mix the flux and lead with spatula with the charge.

CUPELLATION

Cupels are best made by a cupel machine from perfectly dry cupel bone ash. Cupels so made can be used immediately after manufacture. If water is employed to make the bone ash coherent, cracking is liable to occur on exposure to muffle temperature unless the cupels are dried out very slowly by allowing them to stand in a warm, dry spot, days or weeks according to the amount of water used. When a brand of bone ash makes a dry pressed cupel which is inclined to crack or split, this tendency is overcome by admixture of the unsaturated portion of old cupels or of bone ash which has been heated in a muffle to about 1000° C. Bone ash which evidently has not been completely decarbonized should not be used, because complete oxidation of its content of organic matter requires that the cupels be kept hot for a long period before commencing cupellation, else spurting of molten lead will take place during the operation. When the form of the saturated portion of the cupel shows that lead oxide is not absorbed freely, an unsatisfactory quality of bone ash is indicated. The bottom of the saturated portion of a well-made cupel of bone ash of first class quality is concave in shape, free of knobs or projections, and can be cleanly separated by hand, with exercise of little effort, from the unsaturated portion. The proportion of the different sizes of particles of bone ash is a matter of consequence. Cupels made wholly of very fine particles are apt to be too dense, unless moulded with so little pressure that they are so fragile, that their manipulation must be conducted with great care. Those made entirely of coarse particles (through 40 and left on 60 mesh) have such a rough cup surface that the cupellation loss is excessive and not uniform.

A very satisfactory cupel is made from bone ash which contains approximately 75% of particles which will pass a 100-mesh screen and the remaining 25% finer than 40 mesh.

The following shows the range of screen analyses of samples taken from 28 barrels of the same brand:

	Per Cent.
Left on 40 mesh	0– 8.7
Through 40 left on 60 mesh	2.2– 6.3
Through 60 left on 70 mesh	3.7– 9.6
Through 80 left on 100 mesh	12.5–20.3
Through 100 mesh	59.1–83.2

Samples from seven of the barrels wet-screened through a 200-mesh sieve gave quantities of fine product ranging from 42% to 58%.

Patent and ready-made cupels, in which magnesium or calcium oxides, plaster of Paris, Portland cement or organic matter may enter as constituents, because they will survive shipment, are of use in situations where the manufacture [illegible] laboratory-moulded cupel is impracticable. When silver beads of 997- [illegible]ness are obtained from such cupels, the cupellation loss is usually greater common from bone ash cupels of normal quality.

patent cupels require the higher temperature generally throughout, always finish of the operation, else freezing will take place, or beads will be [illegible]ed which may retain quite as much lead as will balance the normal loss of

The brands of patent cupels which preserve a smooth, hard surface after cupellation will retain a trace of silver (0.10 milligram or less) in easily discoverable form. This amount is difficult to find in a bone ash cupel unless made entirely or cup finished with a grade of very fine quality.

While a bone ash cupel absorbs practically its own weight of lead in the form of lead oxide, it is well to make the size such that the saturated portion will not reach quite to the bottom. A cupel $\frac{3}{4}$ in. in height, 1 in. in diameter is suitable for a 12-gram button; 1 in. in height, $1\frac{1}{8}$ ins. diameter for a 20-gram button; 1 in. in height $1\frac{1}{4}$ in diameter for a 25-gram button.

The cup of the cupel should be perfectly smooth and free of any particles of loose bone ash. Such particles as may adhere may be removed by blowing on them. Loosening the particles by the finger may roughen the surface and increase the cupellation loss.

The lead button is prepared for cupellation by freeing it all of adherent particles of slag. Presence of slag corrodes the cupel. It is pounded on a smooth anvil with a flat-faced hammer and then shaped into a cube or disk which will fit the cupel and be firmly held by the tongs. It is good practice to round the corners of the button. A soft, brittle button may result, through the presence of lead oxide in its composition, from completion of scorification at too low a temperature. A button containing more than 25% of silver or gold is brilliantly smooth, hard and brittle. Selenium or tellurium in considerable quantity makes the button rough, brittle and difficult to separate from the slag. A small quantity of sulphur will make the surface of the button scale. Arsenic and antimony have a similar effect.

Operation. In a small or low-formed muffle, cupellation of only a single or possibly two rows of cupels placed near the front can be carried out successfully. When cupellation is carried out in a single row near the front, the position and shape of the row is determined by experience. Besides regulation of fuel supply, temperature of the cupel is controlled by placing scorifiers or old cupels in front and back of the row and by manipulation of the muffle door and damper. Large and small buttons can be cupelled simultaneously by this method. Because the action tends to increase silver loss into the cupel, a cupel should not, while cupellation is in progress, be moved in a manner which will cause change of position of the metal in the cup. In a muffle high enough to allow view of metal inside of a cupel placed near the back wall and of size large enough to be unaffected quickly by small heat changes, cupellation is conducted in a series of rows of cupels extending from close to the back wall to within 4 or 5 ins. of the front. To hold the heat in the front and back rows, it is common practice to bank against the cupels in these rows bone ash, old cupels, scorifiers or pieces of thin brick. Some operators make it possible to do very artistic feathering by building a dam of bone ash several inches high near the door of the muffle to break and heat the current of air over the cupels. Cupellation by this method should be of buttons of nearly uniform size.

Entrance of the products of combustion to the muffle retards cupellation.

By nice adjustment of temperature previous to commencement of the operation in a large muffle carrying many cupels, little regulation of the fuel supply is required. Heat effects are produced by manipulation of the muffle door and of $\frac{1}{4}$ in. thick cooling irons with 3-ft. handles. The irons are shovel shaped to cool the entire top of the muffle and of rectangular form to cool a single lateral or longitudinal row. During the early part of the operation heat is supplied and tempera-

ture raised by oxidation of the lead in the cupels. Toward the end of the opera tion, the rise of temperature produced by moderate reduction of the rate of flo of air through the muffle, together with the heat retained by the closely packe cupels is usually sufficient to produce silver beads of standard purity, when th cupels are of good quality.

Previous to commencement of the operation, to expel moisture, burn organi matter, decompose $CaCO_3$ in the cupels, to give them time to gain a temperatur uniform with the atmosphere of the closed muffle and to permit the furnace a a whole to acquire a condition of temperature and equilibrium of flow of heat whic will allow control of muffle temperature without application of extreme method of heating or cooling; the cupels in the tight muffle should be brought to an allowed to remain for at least ten minutes at a temperature only very little abov that which will cause scum of oxide on the surface of molten lead to melt and b absorbed by the cupel material.

"The temperature of cupellation of pure lead buttons should be 850° C. t uncover the button; this may be lowered to 770° C. during the major part of th cupellation, but must be raised to about 830° C. near the end to finish the opera tion." [1]

The muffle damper being closed, the lead buttons are placed in the cupels in the order of the numbers on the scorifiers in a tray. The muffle door is closed until the lead in all the cupels will "uncover" or "drive." Immediately the damper is opened somewhat.

The temperature of the top of the cupel is then cooled by the methods mentioned until the appearance of the margin of the molten metal within the cupel and the color of the saturated portion of the cupel indicates to the experienced operator that a fringe of crystalline or "feather" litharge is forming just above the lead. If the cooling is carried too far, the cupel becomes too cold to absorb the litharge and "freezing" is the result. Approach to this condition is manifested by the tendency of the line of juncture of metal and cupel to appear indefinite. If, in an attempt to raise the temperature of a charge of cupels, the flow of air through the furnace is stopped, cupellation will cease because a coating of solid oxide will form on the surface of the lead which will require a considerable rise of temperature to melt. The operation of alternately cooling and allowing the temperature to rise is continued until little lead remains. As the quantity of lead and the heat imparted to the cupel through its oxidation diminishes, the temperature of the cupel must be increased until at the moment when the silver-gold bead is practically free of lead, the temperature should be close to that at which cupellation was started. If the temperature is too high at this moment the silver bead will not at once solidify and while molten will asborb oxygen. When the bead solidifies, the oxygen is expelled with the projection of rough points on the bead and sometimes of particles entirely separate from the bead. The tendency to "sprout" or "spurt" increases with the size of the beads. When a cupel is kept in a muffle at a high temperature for a considerable period previous to commencement of cupellation, the silver bead exhibits a tendency to remain liquid at a temperature far below the normal freezing-point of silver. The same inclination is also quite characteristic of cupellation in a dense cupel of fine bone ash. When such a bead solidifies the expulsion of oxygen has been known to be so violent as to break the beads apart. When a bead is induced to become solid by taking the cupel out of the muffle and giving it a series of shocks, if sprouting does not take place,

[1] Fulton, "Fire Assaying," 2d ed., 41.

the bead is often found to be hollow. Silver loss tends to increase with length of time that the bead remains in a state of suffusion. Rootlets extending into the cupel are peculiar to beads which have been in this state. A silver bead having once solidified in its cupel does not require immediate removal from the furnace, but may remain for any reasonable period without loss or gain of weight, providing the temperature of the cupel is not raised so high that its fringe of feather litharge is melted. If the temperature is too low during the oxidation of the last portion of the lead, "freezing" with accumulation of unabsorbed litharge is likely to occur. Solidification of a lead silver alloy which forms a flat dull-colored bead with smooth under surface and is non-adherent to the cupel, may sometimes occur. This alloy may contain as much as 10% of lead. Because the heat of oxidation of copper is greater than that of lead, freezing is less likely to occur in the cupellation of buttons containing no greater quantity of copper than is suited to the process.

Except when the bead contains more than 20% of gold, it should be silvery white, globular and, when hot, adherent to the cupel. As the ratio of gold increases, unless the cupellation is finished at a high temperature, the bead is apt to be dull on account of retained lead, or copper when that metal is present in the button.

An indented bead if silvery white is not an indication of impurity, but if the luster is dull the presence of bismuth, copper, selenium or tellurium may be suspected. Bismuth in moderate quantity (a few tenths per cent of the lead alloy) is taken up by large beads to such an extent that the bismuth content may more than balance the excessive cupellation loss on account of its presence. Through the inclination to leave particles of the precious metal on the sides of the cupel, the excessive loss may exhibit itself in the case of small beads. Copper being absent, bismuth produces a brownish stain under the silver bead and dark green rings about it. When a large quantity of bismuth, selenium or tellurium is present the surface tension of the silver bead is diminished to such an extent that it may spread over the surface and into the bottom of the cupel. These impurities in lesser quantity modify the appearance of the silver bead according to the amount of silver and the finishing temperature of the cupellation. In the assay for gold, the result obtained from parting the product of cupellation of a tellurium-bearing bead is usually higher than that obtained by removal of tellurium by wet methods. Recupellation is of necessity occasionally resorted to in order to obtain a silver bead sufficiently pure to favor the production of a gold mass which can be collected in the process of parting.

The presence of a large proportion of silver decreases the gold loss especially in the cupellation of buttons containing selenium or tellurium. In the assay for silver and for silver and gold in bismuth-bearing material, selenium, tellurium and bismuth should be separated by the combination method described on page 772.

Copper eliminated before the last of the lead causes no abnormal cupellation loss. When its proportion in the lead button is large enough to extend the dark stain on the cupel to the seat of the bead, but insufficient to prevent cupellation with "feathers," the cupellation loss is somewhat more than normal when the final temperature is hot enough to bring about a bead of standard purity. But if the ratio of gold to silver is low in the bead or the final temperature is not high, copper may be retained in the bead in quantity sufficient to offset a part or more than the whole of the abnormal amount of silver absorbed. No attempt should be made to cupel a lead button containing a greater proportion of copper than will allow cupellation with "feathers." Antimony to the extent of 2% may be present

in the lead button.[1] A large quantity produces scoria and causes cracking of the cupel. The presence of antimony and any of the base metals whose oxides are not very soluble in lead oxide causes large and not uniform loss of the precious metals into the cupel because of the high heat required to start and sometimes to continue cupellation, and through retention of particles in the scoria of oxide about the sides of the cupel.

The presence of platinum or palladium raises the temperature of the melting-point of the silver-gold alloy and increases the tendency to retain lead by the product of cupellation. The presence of but a very small proportion of either gives a steely hue to the silver bead. With increase of proportion of the platinum

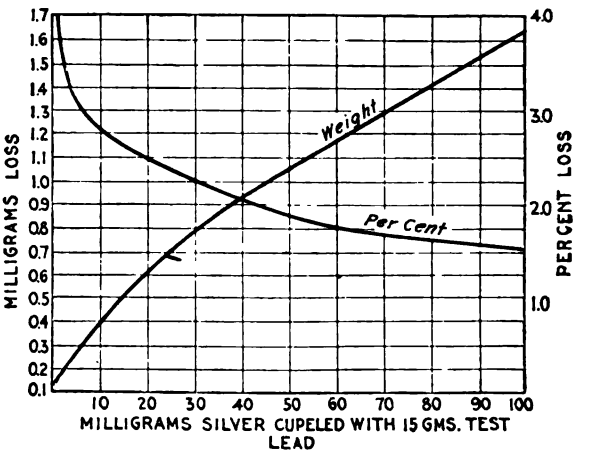

FIG. 141.

metals and influenced by the final temperature of cupellation, the bead becomes flat, its surface dull, crystalline, rough or irregular and its color gray or almost black. The effect of either metal alone is similar but not exactly alike. Palladium shows a tendency to produce beads of less luster, darker in color and of more irregular surface.

Since the freezing-point of the silver-gold alloy increases rapidly with the percentage of gold, care is required when the ratio of silver to gold is less than 6 to 1, that the final temperature of cupellation be higher than is required to obtain a gold-free silver bead of standard purity.

Loss of both gold and silver into the cupel increases with the quantity of lead used. Custom and convenience have made it the very common practice to carry out cupellation on buttons of 15 to 25 grams, resulting from crucible fusion, and on those between 10 and 20 grams which are the product of scorification. Amount of lead remaining constant, cupellation loss of silver decreases in percentage with increase of quantity. Chart Fig. 141 is the product of several hundred cupellations, chiefly of pure silver, made in the course of trials of different brands and graded mixtures of bone ash and other experiments. The lead used was reduced from litharge made from the best grade of test lead; 200 grams gave an unweighable amount of silver and bismuth. The beads assayed 996.5–998 fineness.

[1] E. A. Smith, "Sampling and Assaying of Precious Metals," 168.

Temperature higher than is required to produce "feather" litharge increases the loss of silver and gold. The effect, however, of temperature of cupellation on small quantities of gold alloyed with silver is so little that ordinarily when the assay is for gold alone care is only taken that the bead does not "spurt."

Weighing the Beads. Error may be introduced in the assay for silver through lack of care in cleaning particles of bone ash from the bead. The bottom of the bead held firmly by pliers is scoured with a bristle assay brush before weighing. Weighing of the silver bead is made to the tenth or twentieth milligram and on a button or assay balance sensitive to one or two hundredths of a milligram. In the assay of low-grade material, appraised in large parcels, and when the accuracy of the method warrants such action, weighings are made to the hundredth milligram on a gold assay balance.

To check balance and mathematical errors it is common practice to weigh and record separately each bead and then the combination of all the beads from the same sample.

Direct cupellation is applied to the assay for silver in lead, and preliminary assay of base and Doré bullion, when no sulphur- or scoria-forming metals and but a few hundredths per cent of selenium and tellurium enter into their composition. When such impurities are present in lead bullion, 10 grams each of lead and litharge and 2 or 3 grams borax-silica flux are added and the test portion subjected to long enough scorification to produce a 15-gram button whether 1 or ½ A.T. be taken for the assay portion.

Lead bullion which contains no impurity interfering with cupellation is cupelled in portions of ½ A.T. each. Each portion is wrapped in a 2-in. square of assayer's sheet lead which weighs about 7 grams. Cupellation is carried out under conditions which favor the production of feather litharge. Correction for slag and cupel loss is applied in the assay of lead bullion usually by direct assay of cupel and slag, but sometimes from the loss sustained by a similar and known quantity of silver cupelled or scorified at the same time and under exactly the same conditions.

Cupellation of base or Doré bullion is most commonly practiced to prepare the assay portion for the parting process, and as a convenient method of making the trial assay preliminary to performance of some form of the Gay-Lussac method of determination of silver. Settlement assays for silver are, however, sometimes made on the purer grades of bullion by the cupellation method.

A preliminary assay of 500 milligrams of the sample is made by wrapping that quantity with 15 or 25 grams of assayers' sheet lead and cupelling with feathers if possible. The experienced operator judges from the quantity of silver and gold present, from the stain on the cupel and from the appearance of the bead, how much copper is present and how much lead to add. To prevent "spurting" some prefer to add a definite amount (less than 10%) of copper to bullion which contains none. The suitable amount of lead to employ in the cupellation may be calculated by multiplying the copper present in grams by 100 and adding 2 when the copper is less than 20% of the bullion; multiplying by 40 and adding 8 when the copper content is between 20 and 60%; multiplying by 20 and adding 14 when the per cent of copper is over 60. As an illustration, a 500-milligram assay portion containing no copper is cupelled with 2 grams lead, while such containing 50, 200 or 450 milligrams of copper would be cupelled with 7, 16 and 23 grams of lead respectively. One or two check portions are made containing the same amounts of silver, gold and copper as were determined by the preliminary assay. In making up the checks, the silver weighed up in the preliminary assay is corrected for cupellation loss by adding in the case of base bullion 1.25% to its weight. Gold under 1% of the silver is not ordinarily included in the check assays when silver only is to be taken account of.

The check and two or more assay portions are cupelled each with the same amount of lead at the same time and under as precisely the same conditions as it is possible to obtain. In calculating fineness the average of the silver and the gold found in the

assay portion is corrected by the actual loss or gain sustained by each precious m in the check portions.

In making the cupellation, conditions of temperature and draft which will s all the cupels uniformly are sought rather than the production of feather lith The temperature, however, should not be so high that the beads are likely to sp Less confidence is placed in results from check portions which show a gain than in t which show a loss, when it is apparent that the loss is not mechanical.

PARTING

To the process of separating gold from silver in such form that it can be lected and weighed with certainty and facility, the action of suitably diluted n acid is better adapted than that of sulphuric acid. On account of the solub of platinum in its silver gold alloy by nitric acid, parting with hot sulphuric is used only when the assay is intended to include that metal. Except by emp ment of methods of manipulation and treatment practice, in the assay of bullion, silver does not dissolve with sufficient completion from beads in wh the ratio of silver to gold is less than 4 or 5 to 1. When this ratio is nat to the material undergoing assay, the bead, after weighing, may be cupelled several grams of lead after addition of about 10 parts silver. It is the be and more commonly followed procedure when low ratios prevail, because a h proportion of silver in the bead tends to prevent gold loss into the cupel, to m a separate assay for gold, and add about ten times as much silver as gold pres to the assay portion at some period previous to cupellation.

Nitric acid and water used in parting should be free of any form of chlor or other halogen, and of the presence of another acid. The gold mass in operation is somewhat more conveniently handled if the silver bead be flatte somewhat. But flattened buttons containing large amounts of gold (over milligrams) appear to require annealing to obtain an uniform parting loss. T gold mass is less liable to break up if the bead is dropped into hot than into c acid. It is more apt to be coherent when the silver is dissolved in a high than a low column of acid. On account of the solvent action on gold in spongy fo by hot nitric acid of a strength approaching 1.42 sp.gr., parting solutions sho never be allowed to become so highly concentrated.

The following methods are employed in a laboratory which has inves gated the solvent effect of the acids and the purity of the gold masses p duced. All the heating operations are conducted on a ¾-in. copper pl covered with strips of asbestos paper and heated by lateral rows of perfora pipe burners. The gas supply to each burner is separately controlled. The sil bead containing less than 2 milligrams of gold is dropped into 25 cc. of hot a of 1.07 sp.gr. (1 part 1.42 sp.gr. acid and 6 parts water) in a 1 oz. casserole and liquid is kept a little below the boiling-point for forty minutes. The gold m is washed with water by decantation three times, dried and annealed by pl ing the casserole over a Bunsen flame until change of color of the mass. A sil bead containing more than 2 milligrams and less than 10 is dropped into 25 of hot acid of 1.04 sp.gr. (1 part strong acid and 9 parts water) in a 1-oz. casser When visible action has ceased, the silver solution is decanted, the casserole fil up with acid of 1.16 sp.gr. and the gold mass digested for fifteen to twenty minu at a temperature a little below the boiling-point. When the quantity of g is more than 10 milligrams, the two-strength acid treatment is carried out i 2-oz. parting flask. During the final treatment the acid is kept boiling gen for twenty minutes. After decantation of the acid liquid, the flask is filled

to the brim with water, the brim closed with the cup of a 1-oz. casserole, the flask quickly inverted and tapped to dislodge particles of gold from the side. The flask is raised until the brim is near the surface and removed with a quick motion to the side. The gold mass is then washed, dried and annealed.

When platinum and palladium are present the gold mass is apt to break up into dark-colored particles, coarse or very fine, according to the proportion of the platinum metals. Selenium or tellurium in the bead will also produce a similar effect. When gold only is to be determined, the single 1 to 6 acid treatment in a casserole is pursued; but if platinum is to be determined the parting with 1 to 6 acid takes place in a flask or covered beaker. The residue is transferred to a filter, about 20 parts of silver added, the filter, covered with 25 grams of lead in a small scorifier. is

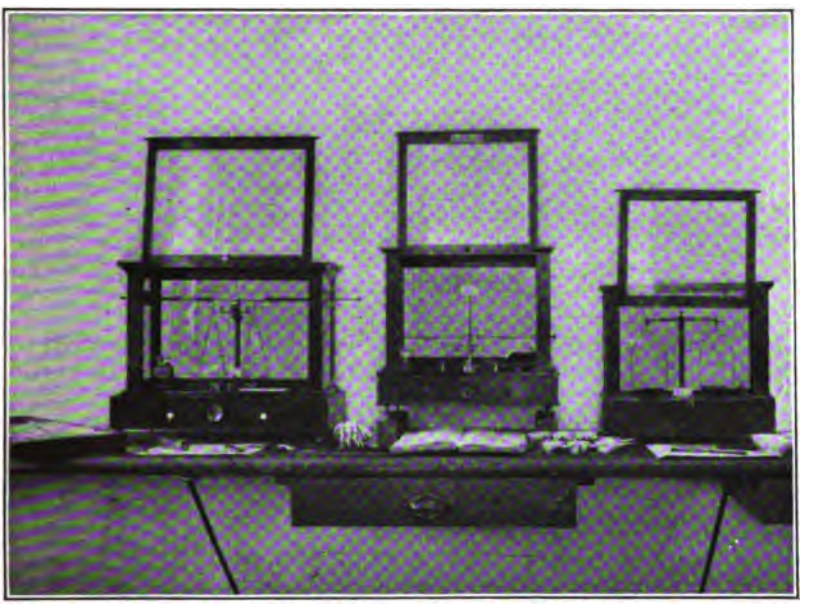

FIG. 142.

incinerated, scorified, cupelled and parting repeated. These operations may require repetition several times before the coherency and color of the gold mass indicates absence of platinum. The presence of even 0.05 milligram of palladium gives a yellow hue to 20 cc. of parting liquor.[1]

Gold is usually weighed to hundredths milligram. When the demand, the sensitiveness of the balance and the accuracy of the method of assay warrant such procedure, weighings to thousandths milligram are made. The low-column type of gold balance is in every way superior to the high. The weights and riders employed should be frequently checked by a set which has been verified

[1] For methods of treatment of the parting liquor for determination of platinum refer to chapter on Platinum, also see article by A. M. Smoot, Eng. and Min. Jour April 17, 1915.

by the Bureau of Standards.[1] To lessen balance and other errors, it is common practice to obtain the weight of each in turn and finally all of the gold masses from the same sample without removal of any from the balance pan.

Gold Bullion. A preliminary assay of 500 milligrams is made to determine very closely the gold and silver content. The weighed quantity of standard silver to be added to make the ratio of silver to gold in the trial assay between 2.5 and 2 to 1, can usually be judged from the color of the gold. When the gold contains no copper, 50 milligrams should be added and the same quantity used in the final assay. The function of the copper is to toughen the gold silver alloy and make possible its reduction by jewelers, rolls to sheet form without cracking. The cupellation of the trial assay is with 10 grams of lead and at a temperature slightly above that which will obtain feather litharge. The button is thoroughly cleaned with a button brush, weighed and rolled into a fillet about 2 ins. long. During rolling, softening or annealing by heating to dull redness may occasionally be required to prevent cracking. The fillet is finally annealed, rolled into a " cornet " and parted in a parting flask by digestion for thirty minutes with 25 to 30 cc. of 1.16 sp.gr. acid at just under the boiling-point. The solution of silver is decanted and washed once by decantation, 25 to 30 cc. more of 1 to 2 acid are added and digestion continued for thirty minutes longer. The gold is transferred to a porcelain casserole in the manner already described, washed by decantation several times, dried and annealed. If the attempt is made to dry the gold mass on a too hot plate, particles are liable to be scattered. The weight of the gold found and that of the added silver subtracted from the weight of the bead is closely the silver content of the bullion. The silver plus the gold content subtracted from the amount of bullion taken for the trial assay gives approximately the quantity of base metal present. When copper is present in a bullion or alloy containing much base, it should be determined by separate analysis.

To two or more assay portions of 500 milligrams each are added just the amount of proof silver determined by the trial assay to make the ratio of silver to gold 2 to 1. If the base does not consist of copper such is added sufficient to make the total 10% of the gold present. One or more check portions are made containing the same amount of gold, silver and copper as are in the assay portions. Each of the check and assay portions are wrapped with exactly 10 grams of lead and cupelled under precisely the same conditions at a temperature somewhat higher than will produce feather litharge. If the bullion contains copper, the same quantity is added to the check portions. The quantity of lead to be used in cupellation depends upon, but as in the assay of silver copper alloys is not in direct ratio to the quantity of copper present. The object is not to remove all the copper by cupellation, but to leave just so much as will toughen the silver gold alloy. Temperature and draft are factors which affect the elimination of copper.

Subject to modification on account of the quantity and character of other impurity, the following table will in a general way serve as a guide to the quantity of lead to use when 500 milligrams of gold bullion are weighed out.

Copper Present in Milligrams.	Lead to Use in Grams.
50	10
100	16
150	22
200	24
250	26
300	28
350	30

The thoroughly cleaned buttons are rolled to the same thickness and length. When cupelled with just the proper amount of copper and lead the edges will not crack. If annealed at too high a temperature the surface will blister and particles are likely

[1] See Circular No. 3, U. S. Bureau of Standards.

to fall off in parting. If the annealing is not uniform or complete, the results will not agree and the value of the check assays is vitiated. The cornets at this point may be stamped by a small die with figures or dots indicating the note-book record of the assay and check portions. Each cornet is then coiled into a roll with index mark outward and placed in a platinum capsule with perforated bottom which will fit the cornets not too loosely or tightly. The capsules set in a platinum tray which has an upright handle and rests on a platinum stand about 1¼ ins. above the bottom of a beaker.

With some experience in soldering platinum with gold and without requirement of much skill, boiling apparatus with capacity for nine tests can be laboratory made from 17 ins. of 0.06-in. wire, nine strips 13 by 31 mm. each of unperforated 0.005-in. sheets, nine circular pieces 10 mm. in diameter and one circular sheet 2 ins. in diameter of 0.005 sheet platinum perforated with 0.062-in. holes, 144 to the square inch. Each capsule is a cylinder 10 mm. in diameter, 13 mm. long, closed at the bottom with perforated metal. To the center of the bottom is soldered a ¼-in. length of 0.06-in. wire. This wire through a perforation holds the capsule upright as it rests on the circular sheet which is soldered to a 2-in. diameter loop in the wire; the wire should extend beyond the loop 1¼ ins. on one side and 6 ins. or more on the other. The sheet in the loop is bent at right angle to the wire and two pieces of wire each 1½ ins. long are soldered to the loops to form a tripod. The wire extending above the frame is bent to form a handle over the side of a beaker and out of direct range of acid fumes.

Two strengths of acids are used, the first of equal parts of 1.42 sp.gr. nitric acid and water the second of 2 parts of acid to 1 of water. The 600-cc. beaker, half filled with No. 1 acid, is brought to boiling, the frame with capsules is slowly introduced to avoid boiling over, and allowed to remain ten to fifteen minutes. The frame is taken out, drained of the acid, dipped in a large beaker of hot water, and then introduced into a beaker half filled with boiling No. 2 acid. After fifteen minutes' boiling the frame is removed, dipped successively into two beakers of hot water, boiled for five to ten minutes in a third, dipped in the fourth, drained and dried by placing in an oven or on a hot plate. The contents of each capsule are removed to an annealing cup or porcelain casserole, annealed and weighed to hundredths milligrams. The actual loss or gain sustained by the check portion is added to or subtracted from the assay portions. The corrected results are calculated to parts per thousand and reported as fineness. More confidence is placed in check assays which show a loss when such loss is known to be not mechanical.

COMBINATION METHODS

Copper Bullion. The sulphuric acid method when skillfully carried out gives results for gold in blister and refined copper equal to those by the " all fire, " and for silver the same as the nitric acid combination method. For each test 1 A.T. is placed in a 1000-cc. beaker of resistance glass and shaken with 5 cc. of a solution of mercuric nitrate (mercuric nitrate solution is made by dissolving 10 grams of mercury with the least quantity—about 25 cc.—of hot nitric acid, making the solution up to 1000 cc. Just sufficient nitric acid is added to keep the solution clear). 80 cc. of 1.84 sp.gr. sulphuric acid are added. Some brands of blister, especially such as contain arsenic, dissolve best when 20 or more cc. of water are also added and the quantity of mercury solution is increased. The beaker covered with a clock-glass is placed on a very hot plate, and boiled vigorously for ten minutes. The temperature is then decreased so low that the accumulation of sulphur on the sides of the beaker will remain, but not so low as to stop quite copious fuming of the acid. The beaker is taken off just before the liquid becomes grayish in color. This point is determined by expert observation of the appearance of the hot solution. The temperature of the hot plate, size of the particles of copper, the quantity and character of impurities in the copper, as well as amount of sulphuric acid used are factors which influence the time required for solution. The time will vary from thirty to ninety minutes. Since the gold is in a very finely divided condition and

a little copper sulphide acts efficiently as an entangling agent, no attempt should be made to continue the treatment with sulphuric acid until the clear liquid, which will result from low silver-bearing copper, indicates complete solution of copper sulphide. Silver sulphide is also effective in preventing gold from passing through the filter, and in the assay of very high gold-bearing copper containing little silver, it is of advantage to add the silver required to carry the gold with minimum loss through cupellation to the beaker before solution rather than to the scorifier or cupel. After the beaker has become cold through standing on an asbestos mat, a little standard salt solution is added to precipitate the trace or more of silver which may be in solution. Although only a trace of silver may be dissolved it is safe to assume that 2% of that present is in solution. At least 600 cc. of boiling hot water are added a little at a time while the lumps of anhydrous salt are being broken up by a stirring rod. The liquid is filtered hot through three or four 15-cm. No. 1 F Swedish filter paper folded together in a funnel (2¾ to 2⅞ ins. in diameter) whose brim is about ¼ in. below the edge of the paper. During filtration copper sulphate must not be allowed to stretch the pores of the paper by crystallizing. Solution, therefore, should be maintained by addition of hot water to the contents of the funnel as required. The beaker is wiped very thoroughly with a piece of common filter paper. The inside of the filter is sprinkled with 15 grams test lead. The filter is folded, placed in a 2½-in. scorifier and covered with 15 grams more lead. The filter is incinerated in an oven or muffle. After adding a pinch (about 2 grams) of borax or borax silica flux, scorification is continued to production of 10- to 15-gram button.

The nitric acid method of solution of blister or other copper is resorted to when the sample is in such coarse form that the sulphuric-acid method is impracticable. The results for gold tend to be lower than those from the sulphuric-acid method, partly because of the solvent action of nitric acid, which is especially noticeable when the copper contains selenium and partly on account of the very fine state of the liberated particles. The solvent action is hindered by alloying the copper with a considerable quantity of mercury and by dissolving with weak acid. In the assay of copper in coarse form some heat must be applied or stronger acid used to complete the solution, but when the sample is fine the heat of the reaction is sufficient.

One A.T. in a covered 1000-cc. beaker is shaken with 5 cc. of a solution of nitrate of mercury which contains 1 gram of mercury, 400 cc. (or a larger amount if the sample is fine) of water and 100 cc. of nitric acid, sp.gr. 1.42 are added. The beaker is allowed to stand overnight, and in the morning solution is completed if necessary by heating gently on a hot plate. An emulsion of lead sulphate is poured in with constant stirring until a permanent precipitate forms. Ten cc. of thick paper pulp is then stirred in and the beaker allowed to stand for an hour on a plate sufficiently hot to promote circulation of the liquid. Filtration is through two 15-cm. papers of S. & S. No. 590 quality. The beaker is wiped thoroughly after taking care to transfer to the filter every trace of the mercury flour which sometimes forms. The inside of the paper is sprinkled with 7½ grams test lead. The paper is folded and placed in a 2½-in. scorifier, the cup of which has been glazed with lead silicate or borate; 7½ grams of lead are placed on the paper, which is then incinerated. To the filtrate with constant stirring is added saturated salt solution—a few drops at a time—until a permanent precipitate remains. The beaker is heated nearly to boiling and more salt solution added in the same way if the precipitate first formed dissolves. When the silver has become granular,

digestion on the hot plate is stopped and the liquid cooled to room temperature before filtering through a single 15-cm. paper of No. 590 quality. When the quantity of silver is high (200 milligrams or over), the copper solution is filtered without disturbing the precipitate. The precipitate is washed quite free of copper by decantation. 7½ grams of lead are stirred into the precipitate and allowed to remain until the appearance indicates that all the silver chloride is reduced. The contents of the beaker are then transferred to the filter. The beaker and stirring rod are thoroughly wiped with filter paper. When the silver tenor of the sample is low, the inside of the paper is sprinkled with 7½ grams of lead. The paper is folded, placed on the residue of the paper containing the product of the previous filtration, covered with 7½ grams of lead and incinerated. Scorification when lead sulphate is present should commence at rather high temperature.

Copper Matte. The following combination method of assaying iron-copper matte gives results for gold equal to that from any of the all-fire methods. One A.T. in an 1000-cc. beaker is gently boiled with 350 cc. of a mixture of 1 part concentrated sulphuric acid and 10 parts water. Boiling is continued until but little gas is given off. The solution is then filtered through a single 15-cm. paper and the residue washed with hot water twice. The filtrate is discarded. The filter paper and its contents are placed in the beaker. Twenty cc. of a solution of mercuric nitrate containing 200 milligrams of mercury are poured over the residue and the beaker immediately shaken until all its particles are wet by the mercury. 150 cc. of water and 100 cc. of nitric acid are added and the beaker allowed to stand for at least half an hour. The liquid is then boiled until no fumes are given off. The solution is then filtered through two 15- cm. filters of No. 589 quality folded together. The beaker is wiped thoroughly with filter paper. The bulky precipitate, sprinkled with 20 grams lead, is placed in a 3-in. Bartlett-shaped scorifier which has been glazed with lead silicate. The folded paper is covered with 20 grams lead, incinerated, fluxed with 2 grams of borax and scorified to a 10-gram button which is reserved for addition to the scorifier containing the silver residue. Scorification should commence at a high temperature. Silver is precipitated as chloride and manipulated in the same manner as has been described in the nitric acid method for blister and refined copper. The total charge of lead in the 2½-in. scorifier containing the silver residue after addition of the button containing the gold, is 25 to 30 grams.

On account of slow filtration, slag in matte interferes with the operation of this method.

The following method of treatment of matte tends to give higher silver but lower gold results. To 1 A.T. in a 1000-cc. beaker are added cautiously at first 100 cc. strong nitric and then 50 cc. conc. sulphuric acid with beaker covered, the liquid is boiled until the sample is completely decomposed and the precipitated sulphur is yellow. When the liquid is cold, the salts are dissolved with 400 cc. hot water and the solution is filtered hot. The procedure from this point is the same as described in the nitric acid treatment of blister copper.

Silver Slime for Gold and Silver. Each assay portion of 0.1 or 0.05 A.T. is wet in a 1000-cc. resistance-glass beaker with 10 cc. of a solution of nitrate of mercury which contains 10 milligrams of mercury. Fifty cc. of 1.84 sp.gr. sulphuric acid are added and boiled for about thirty minutes. When cold, 400 cc. of hot water are added and after all salts are in solution, a solution of sodium chloride of approximately known silver precipitating strength is dropped in with constant stirring until it is evident that a slight excess has been added. The liquid is stirred

until silver chloride is coagulated. When cold, the clear liquid is decanted through a 15- cm. No. 589 paper without disturbing the precipitate. The precipitate is washed free of copper by decantation. Ten grams of 40-mesh test lead are sprinkled over the inside of the filter. Twenty grams of test lead and a few drops of a solution of sodium sulphide are mixed with the precipitate of silver chloride with a stirring rod. When it is apparent that reduction of silver is quite complete the residue is washed into the filter and the beaker thoroughly wiped with filter paper. After draining the filter is folded, placed in a 3-in. scorifier, covered with 10 grams of lead, dried and incinerated. Fluxed with a pinch (2 to 3 grams) of borax glass, scorification is continued to production of a 15- to 20-gram button. Corrected assay is made of the slag and cupel.

Removal of Interfering Metals. Inasmuch as bismuth, selenium or tellurium are not readily removed from a lead button by dry oxidation, with the object of avoiding repeated scorifications, it is expedient to remove these elements by dissolving the well-cleaned lead button with twelve times as many cc. as its weight in grams of a mixture of 1 part of strong nitric acid with 5 parts water. The gold is filtered, the silver precipitated, reduced when high, filtered and the filters containing each of the precious metals manipulated as has been described. In the treatment of a bismuth-bearing button, the filter should be washed with acidulated water. When platinum is present in the material undergoing assay in quantity sufficient to interfere with the purity of the silver bead produced by cupellation at the usual temperature, the solution of the lead button by nitric acid is filtered through a small filter. The content of the thoroughly washed filter is treated for determination of platinum and gold by methods described in chapter on Platinum. Silver in the filtrate is precipitated as chloride and determined by the described procedures of filtration, scorification and cupellation. By this method may be conducted the assay for silver in material containing gold in excess of silver.

When the precipitate of silver chloride is colored a deep pink, indicating the presence of considerable palladium, the button resulting from its scorification is dissolved, silver again precipitated, filtered, scorified and, if the silver chloride is not too highly colored, cupelled.[1]

Assay of Cobalt—Silver Ore.[2] ¼ or ½ A.T. portions are taken, the former when the sample carries over 2000 oz. silver per ton. Nitric acid is added a little at a time to the pulp in a covered beaker, about 75 cc. for a ¼-A.T. or 100 cc. for a ½ A.T. portion. After heating on a steam bath until action has ceased, 200 cc. water are added and the solution allowed to stand (best over night) until cold before filtration. From some ores containing much arsenic, a white crystalline coating containing a little silver forms, and unless allowed to form in the original nitric acid solution will cause trouble later. If the coating cannot be detached by filter paper it is treated in the beaker with a hot solution of sodium hydrate. The alkaline liquid is acidulated with nitric acid and washed into the filter with the insoluble residue. If the insoluble residue is large in volume, it is dried, burned in a crucible and fused with litharge, borax, sodium carbonate and a reducing agent. If the residue is small, it is scorified. In either case the lead button from the residue is reserved.

Standard sodium chloride solution is added to the filtrate from the insoluble residue in quantity sufficient to precipitate all the silver, but carefully avoiding

[1] See article by A. M. Smoot, End. and Min. Jour., April 17, 1915, p. 701.
[2] Smoot, Eng. and Min. J., 28, 1100, 1914.

any considerable excess. The precipitate is stirred briskly until it coagulates and then is allowed to stand for an hour until the supernatant liquid becomes clear. The precipitate is transferred to a double filter and washed slightly with water. Traces of silver chloride in the beaker are wiped off with filter paper and placed in the filter. The filter is transferred to a scorifier which has been glazed with molten litharge. As a further precaution against absorbing moisture, a small disk of lead is placed under the paper. The paper in the scorifier is dried and burned in a closed oven at 250 to 300° C. Fine test lead is sprinkled over the residue and the button resulting from the crucible or scorifier fusion of the insoluble residue is added. Scorification at a low temperature is conducted to production of a 15-gram button which is cupelled with care to avoid " sprouting." The influence of bismuth which cobalt ores sometimes contain is eliminated by the combination method.

CYANIDE SOLUTIONS

Inasmuch as cyanide solutions have but little greater gravity than water, 29.2 cc. is regarded as the volume equivalent of 1 A.T. The quantity taken for assay depends upon the gold or silver content; 1 A.T. of a rich solution, 50 to 100 A.T. when traces of the metals are sought; 5, 10 or 10 A.T. are the test portions most commonly employed. When gold only is to be determined, there should be in the lead button prepared for cupellation sufficient silver to permit parting of the bead resulting from the operation. Silver may be added to the button or solution in the form of metal or to the solution in the form of a standard solution of silver nitrate if the electrolytic or evaporation method is employed.

The methods of preparation of the solution for fire assay may be grouped as follows:

(*a*) ***Evaporation.***[1]

(*b*) ***Metallic Reagent.***[2] Aluminum foil,[3] cement copper,[3] zinc dust, zinc lead couple formed by the addition of lead acetate to the cyanide solution and precipitation of spongy lead by zinc shavings,[4] by zinc dust,[5] by stick zinc,[6] aluminum-lead couple.[7]

(*c*) ***Electrolytic.***[8]

(*d*) ***Liquid reagent,*** potassium ferrocyanide and cuprous chloride,[9] copper sulphate and sodium sulphite,[10] ferrous sulphate, oxalic acid.

(3) ***Gaseous reagent,*** hydrogen sulphide.[11]

The evaporation method is the standard with which all other methods are compared, and on account of the requirement of little manipulation, is practiced

[1] All Manuals or Text Books of Assaying.
[2] Seamon, West. Chem. and Met., Aug., 1909, 291.
[3] Arents, Trans. A.I.M.E., 34, 184.
[4] Chiddy, Eng. and Min. J., Mar. 28, 1903, 473.
[5] Magenau, Min. and Sci. Press, Apr. 14, 1906, 259; Stines, Min. and Sci. Press, Apr. 28, 1906, 278; Durant, Proc. Chem. Met. and Min. Soc. of S.A., 1902–3, 105; Clark, Fulton's " Manual of Fire Assaying," 2d ed. 156.
[6] Bahney, Trans, A.I.M.E., 51, 131.
[7] Holt, Min. and Sci. Press, June 11, 1910, 863.
[8] Miller, J. Chem. Met. and Min. Soc. of S. A., Feb. 15, 1905, 216; Crichton, J. Chem. Met. and Min. Soc. of S. A., 1911–12, 90.
[9] White, J. Chem. Met. and Min. Soc. of S. A., Oct., 1909, 136.
[10] Whitby, Proc. Chem. Met. and Min. Soc. of S. A., 1902–3, 15.
[11] Watson, Eng. and Min. J., Mar. 28, 1911, 443.

with considerable variety of detail in laboratories which make a large number of assays. From a 6- by 4-in. strip of assayers' sheet lead, a flat-bottom dish 4 by 2 by 1 in. deep can be made, which will weigh 30 to 40 grams and hold 3 A.T. A test portion of this or a larger amount of cyanide solution introduced from time to time is evaporated to dryness. To avoid spattering the heat of the hot plate is reduced toward the last of the operation. The dish is folded carefully and scorified to a 15- to 20-gram button in a 3-in. scorifier. A 10 or 20 A.T. test portion may be evaporated to small volume in an evaporating dish or casserole, and then to dryness in a lead dish. When it is the practice to complete the evaporation in porcelain or earthen ware, 50 to 60 grams of litharge are added with the object of facilitating removal of the residue. The residue, which should not be heated so strongly as to make a hard cake, is removed with a spatula and intimately mixed with a charge [1] consisting of 25 grams litharge, 15 grams sodium carbonate, 2 grams fine silica, 5 grams borax glass and 2 grams argol. Fusion is made in a 20-gram crucible. When the scorification method of fusion is preferred, 10 grams of granulated lead are added to the solution instead of litharge, the residue transferred to a 2-in. scorifier, covered with 15 grams test lead and a pinch of borax glass and scorified to a 15- to 20-gram button. Whether litharge or lead is used, the dish should be wiped thoroughly with moist filter paper which is placed in the bottom of the crucible or retained in place in the scorifier by the 15 grams of test lead.

Of the metallic reagent methods, the zinc-lead couple is most commonly practiced. The details of manipulation vary with different operators. The following method combines the features of Clark's [2] and Bahney's.[3] To the test portion of cyanide solution in a beaker of capacity several hundred cc. in excess of its liquid content, are added 25 cc. of a 20% solution of lead acetate. From a bottle having a ⅛-in. glass tube through the stopper and holding silver-free zinc dust and water in the proportion of 1 gram in 3 cc., the equivalent of 4 grams of dust is shaken out into a suitable graduate and added to the cyanide liquor. When moderately heated, but before boiling, a volume of 1.18 to 1.19 S.G. C.P. hydrochloric acid equal to 10% of the cyanide solution is added. The mixture is then boiled not too vigorously until the spongy lead aggregates (five to ten minutes).

Since some zinc may remain undissolved in the mass above the surface of the liquid, after removal of the beaker from the hot plate, the precipitate is collected and confined below the surface by an overturned funnel which has a diameter 1 in. less than the diameter of the beaker and whose constricted throat is sealed with a small ball of barren lead sponge. After standing hot for five to ten minutes the funnel is removed and washed free of adherent particles. The beaker is then filled up with cold water. From a circular piece of assayers' sheet lead 3 ins. in diameter and weighing 7 to 9 grams a filter cone is made by pricking a dozen fine holes through and about the apex. This cone is fitted to a 2-in. funnel in a filter flask which is connected to aspirating apparatus. A layer of 5 grams of test lead, finer than 60 mesh, is shaped over the perforated portion of the cone. The clear liquid is decanted as completely as is practicable without loss of precipitate. The beaker is again filled with cold water and decanted. A portion of the sponge is drawn with the flattened end of a glass rod onto the filter cone and tamped into

[1] Fulton, "Manual of Fire Assaying," 2d ed., 157.
[2] Fulton's "Manual of Fire Assaying," 2d ed, 156.
[3] Trans. A.I.M.E., 51, 129.

place. After complete removal of the precipitate to the cone, it is washed several times and then dewatered by tamping with the rod. The edges of the filter cone are folded tightly over the precipitate to form a cone-shaped button which will fit a 1½-in. cupel. The button is placed in a hot cupel which is brought to the front of the muffle and allowed to remain there no longer than is sufficient to expel moisture. A piece of glowing charcoal placed in front of the cupel will help to clear the lead shortly after the muffle door is closed, if the muffle has been kept at the temperature which prevails in the usual practice of starting cupellation.

If suspended matter insoluble in hydrochloric acid or considerable copper is present in the solution, cupellation without previous scorification is impracticable, the other details of the method, however, may be carried out as described. In such cases the lead button is placed in a 2-in. scorifier, 10 grams of test lead and borax flux are added and scorification continued to production of a 10- to 15-gram button. In case much copper is present, it may be necessary to rescorify with addition of more lead.

By the electrolytic method,[1] gold is deposited on a cylinder of assay lead foil which fits closely the inside and rests on the bottom of the beaker. The lower edge of the foil is serrated to promote circulation. The anode is a $\frac{5}{16}$-in. carbon rod. The current is adjusted to the KCN strength of the solution; 0.1 amp. for a 0.3% to 0.04 amp. for a 0.02% solution. To avoid plating out on the anode, care is taken to have the current on all the time it is in contact with the solution. A little cyanide added to a weak solution facilitates the deposition of gold; and ammonium hydrate is added when the solution is impure. When deposition is complete (four hours), the lead foil is washed, dried, folded into a button and cupelled.

Christy's liquid reagent method, as modified by Whitby and described by Clennell,[2] is based on the fact that when a copper salt together with a reducing agent is added to an acidulated cyanide solution, a precipitate of cuprous cyanide is formed which precipitates silver and all but a trace of gold. To 10 A.T. are stirred in successively 20 cc. 10% solution of blue vitriol, 20 cc. 15% solution of sodium sulphite and 10 cc. 10% sulphuric acid. Addition of a little ferrocyanide of potassium hastens settling. The mixture is stirred thoroughly, allowed to settle for fifteen minutes, filtered and the filtrate refiltered until clear. When drained the precipitate is covered with a mixture of 30 grams litharge, 30 grams borax glass and 1 gram charcoal. The paper and contents are placed in a hot E or F crucible and the operations of fusion and cupellation carried out.

[1] Crichton, J. Chem. Met. and Min. Soc. of S. A., 1911–12, 90.
[2] Cyanide Hand Book, 443.

PART III

TABLES AND USEFUL DATA

TABLES AND USEFUL DATA

I.—INTERNATIONAL ATOMIC WEIGHTS, 1917

	Symbol.	Atomic Weight.		Symbol	Atomic Weight.
Aluminum	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emanation)	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Caesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.005	Praseodymium	Pr	140.9
Cerium	Ce	140.25	Radium	Ra	226.0
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.06
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.00	Thallium	Tl	204.0
Holmium	Ho	163.5	Thorium	Th	232.4
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	118.7
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.2
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.20	Ytterbium (Neoytterbium)	Yb	173.5
Lithium	Li	6.94	Yttrium	Yt	88.7
Lutecium	Lu	175.0	Zinc	Zn	65.37
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Manganese	Mn	54.93			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

II.—MELTING-POINTS OF THE CHEMICAL ELEMENTS[1]

Reproduced from Circular No. 35 (2d edition) of U. S. Bureau of Standards.

Element.	C.	F.
Helium	<−271	<−456
Hydrogen	−259	−434
Neon	−253?	−423
Fluorine	−223	−369
Oxygen	−218	−360
Nitrogen	−210	−346
Argon	−188	−306
Krypton	−169	−272
Xenon	−140	−220
Chlorine	−101.5	−150.7
Mercury	− 38.9	−38.0
Bromine	− 7.3	+18.9
Caesium	+ 26	79
Gallium	30	86
Rubidium	38	100
Phosphorus	44	111.2
Potassium	62.3	144
Sodium	97.5	207.5
Iodine	113.5	236.3
Sulphur	S_I 112.8	235.0
	S_{II} 119.2	246.6
	S_{III} 106.8	224.2
Indium	155	311
Lithium	186	367
Selenium	217–220	422–428
TIN	231.9	449.4
Bismuth	271	520
Thallium	302	576
CADMIUM	320.9	609.6
LEAD	327.4	621.3
ZINC	419.4	786.9
Tellurium	452	846
ANTIMONY	630.0	1166
Cerium	640	1184
Magnesium	651	1204
ALUMINUM	658.7	1217.7
Radium	700	1292
Calcium	810	1490
Lanthanum	810?	1490
Strontium	>Ca<Ba?	

Element.	C.	F.
Neodymium	840?	1544
Arsenic	850?	1562
Barium	850	1562
Praseodymium	940?	1724
Germanium	958	1756
SILVER	960.5	1761
GOLD	1063.0	1945.5
COPPER	1083.0	1981.5
Manganese	1260	2300
Samarium	1300–1400	2370–2550
Beryllium (glucinum)	1350?	2462
Scandium	?	
Silicon	1420	2588
NICKEL	1452	2646
Cobalt	1480	2696
Yttrium	1490	2714
Chromium	1520	2768
IRON	1530	2786
PALLADIUM	1549	2820
Zirconium	1700?	3090
Columbium (Niobium)	1700?	3090
Thorium	>1700	>3090
	<Pt	<Pt
Vanadium	1720	3128
PLATINUM	1755	3191
Ytterbium	?	
Titanium	1800	3272
Uranium	<1850	<3362
Rhodium	1950	3542
Boron	2200–2500?	4000–4500
Iridium	2350?	4262
Ruthenium	2450?	4442
Molybdenum	2500?	4500
Osmium	2700?	4900
Tantalum	2850	5160
TUNGSTEN	3000	5430
Carbon	>3600 for p. = 1 at.	>6500 for p. = 1 at.

III. OTHER TEMPERATURE STANDARDS

Temperatures of Flames.[2]

	Cent.	Deg. of Accuracy.
Bunsen, open	1870	Within 100° C.
Bunsen, half open	1810	Within 100° C.
Bunsen, shut	1710	Within 100° C.
Acetylene	2550	Within 100° C.
Oxyhydrogen with illuminating gas	2200	Within 100° C.
Oxyhydrogen with H_2+O	2420	Within 100° C.
Electric arc	3500	Within 150° C.
Sun	6000	Within 500° C.

[1] Metallurgical and Chemical Engineering, Vol. XIII, No. 5, May, 1915.
[2] Measurement of High Temperatures, G. K. Burgess and H. Le Chatelier.

Approximate Temperatures by Colors.

	Cent.	Fahr.
First visible red	525	977
Dull red	700	1292
Cherry red	900	1652
Dull orange	1100	2012
White	1300	2372
Dazzling white	1500	2732

Substance.	Phenomenon.	C.	F.	Variation with pressure (pressure in mm. of Hg.)
Oxygen	Boiling	−183.0	−297.4	C. °−183.0+0.01258 (p. 760) −0.0000079 (p. 760)
Carbon dioxide	Sublimation in inert liquid	− 78.5	−109.3	C. °=−78.5+0.017 (p. 760)
Sodium sulphate $Na_2SO_4+10H_2O$	Transformation into anhydrous salt	32.384	90.291	
Water	Boiling	100	212	C. °−100+0.03670 (p. 760) −0.00002046 (p. 760)
Naphthalene	Boiling	217.96	423.73	C. °=217.96+0.058 (p. 760)
Benzophenone	Boiling	305.9	582.6	C. °−305.9+0.063 (p. 760)
Sulphur	Boiling	444.6	832.3	C. °=444.6+0.0908 (p. 760) −0.000047 (p. 760)
Ag_2Cu_2	Eutectic Freezing	779	1434	
Sodium chloride	Freezing	801	1472	

IV.—ELECTROMOTIVE ARRANGEMENT OF THE ELEMENTS

Each element is positive to the element placed after it and negative to the element placed above.

1. Cs	14. Al	27. Ge	40. Os	53. Mo
2. Rb	15. Zr	28. In	41. Au	54. V
3. K	16. Th	29. Ga	42. H	55. Cr
4. Na	17. Ce	30. Bi	43. Sn	56. As
5. Li	18. Di	31. U	44. Si	57. P
6. Ba	19. La	32. Cu	45. Ti	58. Se
7. Sr	20. Mn	33. Ag	46. Cb	59. I
8. Ca	21. Zn	34. Hg	47. Ta	60. Br
9. Mg	22. Fe	35. Pd	48. Te	61. Cl
10. Be	23. Ni	36. Ru	49. Sb	62. F
11. Yt	24. Co	37. Rh	50. C	63. N
12. Er	25. Cd	38. Pt	51. Bo	64. S
13. Sc	26. Pb	39. Ir	52. W	65. O

ACID AND ALKALI TABLES

V.—HYDROCHLORIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
1.00	1.0069	1.38	1.40	14.25	1.1090	21.80	21.68
2.00	1.0140	2.80	2.82	14.50	1.1111	22.22	22.09
3.00	1.0211	4.22	4.25	14.75	1.1132	22.64	22.50
4.00	1.0284	5.68	5.69	15.00	1.1154	23.08	22.92
5.00	1.0357	7.14	7.15	15.25	1.1176	23.52	23.33
5.25	1.0375	7.50	7.52	15.50	1.1197	23.94	23.75
5.50	1.0394	7.88	7.89	15.75	1.1219	24.38	24.16
5.75	1.0413	8.26	8.26	16.0	1.1240	24.80	24.57
6.00	1.0432	8.64	8.64	16.1	1.1248	24.96	24.73
6.25	1.0450	9.00	9.02	16.2	1.1256	25.12	24.90
6.50	1.0469	9.38	9.40	16.3	1.1265	25.30	25.06
6.75	1.0488	9.76	9.78	16.4	1.1274	25.48	25.23
7.00	1.0507	10.14	10.17	16.5	1.1283	25.66	25.39
7.25	1.0526	10.52	10.55	16.6	1.1292	25.84	25.56
7.50	1.0545	10.90	10.94	16.7	1.1301	26.02	25.72
7.75	1.0564	11.28	11.32	16.8	1.1310	26.20	25.89
8.00	1.0584	11.68	11.71	16.9	1.1319	26.38	26.05
8.25	1.0603	12.06	12.09	17.0	1.1328	26.56	26.22
8.50	1.0623	12.46	12.48	17.1	1.1336	26.72	26.39
8.75	1.0642	12.84	12.87	17.2	1.1345	26.90	26.56
9.00	1.0662	13.24	13.26	17.3	1.1354	27.08	26.73
9.25	1.0681	13.62	13.65	17.4	1.1363	27.26	26.90
9.50	1.0701	14.02	14.04	17.5	1.1372	27.44	27.07
9.75	1.0721	14.42	14.43	17.6	1.1381	27.62	27.24
10.00	1.0741	14.82	14.83	17.7	1.1390	27.80	27.41
10.25	1.0761	15.22	15.22	17.8	1.1399	27.98	27.58
10.50	1.0781	15.62	15.62	17.9	1.1408	28.16	27.75
10.75	1.0801	16.02	16.01	18.0	1.1417	28.34	27.92
11.00	1.0821	16.42	16.41	18.1	1.1426	28.52	28.09
11.25	1.0841	16.82	16.81	18.2	1.1435	28.70	28.26
11.50	1.0861	17.22	17.21	18.3	1.1444	28.88	28.44
11.75	1.0881	17.62	17.61	18.4	1.1453	29.06	28.61
12.00	1.0902	18.04	18.01	18.5	1.1462	29.24	28.78
12.25	1.0922	18.44	18.41	18.6	1.1471	29.42	28.95
12.50	1.0943	18.86	18.82	18.7	1.1480	29.60	29.13
12.75	1.0964	19.28	19.22	18.8	1.1489	29.78	29.30
13.00	1.0985	19.70	19.63	18.9	1.1498	29.96	29.48
13.25	1.1006	20.12	20.04	19.0	1.1508	30.16	29.65
13.50	1.1027	20.54	20.45	19.1	1.1517	30.34	29.83
13.75	1.1048	20.96	20.86	19.2	1.1526	30.52	30.00
14.00	1.1069	21.38	21.27	19.3	1.1535	30.70	30.18

V.—HYDROCHLORIC ACID (Continued)

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
19.4	1.1544	30.88	30.35	22.5	1.1836	36.72	36.16
19.5	1.1554	31.08	30.53	22.6	1.1846	36.92	36.35
19.6	1.1563	31.26	30.71	22.7	1.1856	37.12	36.54
19.7	1.1572	31.44	30.90	22.8	1.1866	37.32	36.73
19.8	1.1581	31.62	31.08	22.9	1.1875	37.50	36.93
19.9	1.1590	31.80	31.27	23.0	1.1885	37.70	37.14
20.0	1.1600	32.00	31.45	23.1	1.1895	37.90	37.36
20.1	1.1609	32.18	31.64	23.2	1.1904	38.08	37.58
20.2	1.1619	32.38	31.82	23.3	1.1914	38.28	37.80
20.3	1.1628	32.56	32.01	23.4	1.1924	38.48	38.03
20.4	1.1637	32.74	32.19	23.5	1.1934	38.68	38.26
20.5	1.1647	32.94	32.38	23.6	1.1944	38.88	38.49
20.6	1.1656	33.12	32.56	23.7	1.1953	39.06	38.72
20.7	1.1666	33.32	32.75	23.8	1.1963	39.26	38.95
20.8	1.1675	33.50	32.93	23.9	1.1973	39.46	39.18
20.9	1.1684	33.68	33.12	24.0	1.1983	39.66	39.41
21.0	1.1694	33.88	33.31	24.1	1.1993	39.86	39.64
21.1	1.1703	34.06	33.50	24.2	1.2003	40.06	39.86
21.2	1.1713	34.26	33.69	24.3	1.2013	40.26	40.09
21.3	1.1722	34.44	33.88	24.4	1.2023	40.46	40.32
21.4	1.1732	34.64	34.07	24.5	1.2033	40.66	40.55
21.5	1.1741	34.82	34.26	24.6	1.2043	40.86	40.78
21.6	1.1751	35.02	34.45	24.7	1.2053	41.06	41.01
21.7	1.1760	35.20	34.64	24.8	1.2063	41.26	41.24
21.8	1.1770	35.40	34.83	24.9	1.2073	41.46	41.48
21.9	1.1779	35.58	35.02	25.0	1.2083	41.66	41.72
22.0	1.1789	35.78	35.21	25.1	1.2093	41.86	41.99
22.1	1.1798	35.96	35.40	25.2	1.2103	42.06	42.30
22.2	1.1808	36.16	35.59	25.3	1.2114	42.28	42.64
22.3	1.1817	36.34	35.78	25.4	1.2124	42.48	43.01
22.4	1.1827	36.54	35.97	25.5	1.2134	42.68	43.40

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 − 145/Sp. Gr.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

10−15° Bé. − 1/40° Bé. or .0002 Sp. Gr. for 1° F.
15−22° Bé. − 1/30° Bé. or .0003 " " " 1° F.
22−25° Bé. − 1/28° Bé. or .00035 " " " 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
A. G. ROSENGARTEN,

New York, May 14, 1903. *Executive Committee.*

VI.—HYDROCHLORIC ACID

LUNGE AND MARCHLEWSKI

Specific Gravity. $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.
1.000	0.16	1.6	1.075	15.16	163	1.145	28.61	328
1.005	1.15	12	1.080	16.15	174	1.150	29.57	340
1.010	2.14	22	1.085	17.13	186	1.152	29.95	345
1.015	3.12	32	1.090	18.11	197	1.155	30.55	353
1.020	4.13	42	1.095	19.06	209	1.160	31.52	366
1.025	5.15	53	1.100	20.01	220	1.163	32.10	373
1.030	6.15	64	1.105	20.97	232	1.165	32.49	379
1.035	7.15	74	1.110	21.92	243	1.170	33.46	392
1.040	8.16	85	1.115	22.86	255	1.171	33.65	394
1.045	9.16	96	1.120	23.82	267	1.175	34.42	404
1.050	10.17	107	1.125	24.78	278	1.180	35.39	418
1.055	11.18	118	1.130	25.75	291	1.185	36.31	430
1.060	12.19	129	1.135	26.70	303	1.190	37.23	443
1.065	13.19	141	1.140	27.66	315	1.195	38.16	456
1.070	14.17	152	1.1425	28.14	322	1.200	39.11	469

COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID*

Pressure mm. of Mercury.	Per Cent of HCl.	Grams constant boiling distillate for 1 mol. HCl.
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Temperature of constant boiling hydrochloric acid is 108.54° at 763 mm. Specific gravity 1.0962^{25}.

* Hulett and Bonner, Jour. Am. Chem. Soc. xxxi, 390.

VII.—NITRIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.
10.00	1.0741	14.82	12.86	21.25	1.1718	34.36	28.02
10.25	1.0761	15.22	13.18	21.50	1.1741	34.82	28.36
10.50	1.0781	15.62	13.49	21.75	1.1765	35.30	28.72
10.75	1.0801	16.02	13.81	22.00	1.1789	35.78	29.07
11.00	1.0821	16.42	14.13	22.25	1.1813	36.26	29.43
11.25	1.0841	16.82	14.44	22.50	1.1837	36.74	29.78
11.50	1.0861	17.22	14.76	22.75	1.1861	37.22	30.14
11.75	1.0881	17.62	15.07	23.00	1.1885	37.70	30.49
12.00	1.0902	18.04	15.41	23.25	1.1910	38.20	30.86
12.25	1.0922	18.44	15.72	23.50	1.1934	38.68	31.21
12.50	1.0943	18.86	16.05	23.75	1.1959	39.18	31.58
12.75	1.0964	19.28	16.39	24.00	1.1983	39.66	31.94
13.00	1.0985	19.70	16.72	24.25	1.2008	40.16	32.31
13.25	1.1006	20.12	17.05	24.50	1.2033	40.66	32.68
13.50	1.1027	20.54	17.38	24.75	1.2058	41.16	33.05
13.75	1.1048	20.96	17.71	25.00	1.2083	41.66	33.42
14.00	1.1069	21.38	18.04	25.25	1.2109	42.18	33.80
14.25	1.1090	21.80	18.37	25.50	1.2134	42.68	34.17
14.50	1.1111	22.22	18.70	25.75	1.2160	43.20	34.56
14.75	1.1132	22.64	19.02	26.00	1.2185	43.70	34.94
15.00	1.1154	23.08	19.36	26.25	1.2211	44.22	35.33
15.25	1.1176	23.52	19.70	26.50	1.2236	44.72	35.70
15.50	1.1197	23.94	20.02	26.75	1.2262	45.24	36.09
15.75	1.1219	24.38	20.36	27.00	1.2288	45.76	36.48
16.00	1.1240	24.80	20.69	27.25	1.2314	46.28	36.87
16.25	1.1262	25.24	21.03	27.50	1.2340	46.80	37.26
16.50	1.1284	25.68	21.36	27.75	1.2367	47.34	37.67
16.75	1.1306	26.12	21.70	28.00	1.2393	47.86	38.06
17.00	1.1328	26.56	22.04	28.25	1.2420	48.40	38.46
17.25	1.1350	27.00	22.38	28.50	1.2446	48.92	38.85
17.50	1.1373	27.46	22.74	28.75	1.2473	49.46	39.25
17.75	1.1395	27.90	23.08	29.00	1.2500	50.00	39.66
18.00	1.1417	28.34	23.42	29.25	1.2527	50.54	40.06
18.25	1.1440	28.80	23.77	29.50	1.2554	51.08	40.47
18.50	1.1462	29.24	24.11	29.75	1.2582	51.64	40.89
18.75	1.1485	29.70	24.47	30.00	1.2609	52.18	41.30
19.00	1.1508	30.16	24.82	30.25	1.2637	52.74	41.72
19.25	1.1531	30.62	25.18	30.50	1.2664	53.28	42.14
19.50	1.1554	31.08	25.53	30.75	1.2692	53.84	42.58
19.75	1.1577	31.54	25.88	31.00	1.2719	54.38	43.00
20.00	1.1600	32.00	26.24	31.25	1.2747	54.94	43.44
20.25	1.1624	32.48	26.61	31.50	1.2775	55.50	43.89
20.50	1.1647	32.94	26.96	31.75	1.2804	56.08	44.34
20.75	1.1671	33.42	27.33	32.00	1.2832	56.64	44.78
21.00	1.1694	33.88	27.67	32.25	1.2861	57.22	45.24

VII.—NITRIC ACID (Continued)

Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.
32.50	1.2889	57.78	45.68	40.75	1.3909	78.18	63.48
32.75	1.2918	58.36	46.14	41.00	1.3942	78.84	64.20
33.00	1.2946	58.92	46.58	41.25	1.3976	79.52	64.93
33.25	1.2975	59.50	47.04	41.50	1.4010	80.20	65.67
33.50	1.3004	60.08	47.49	41.75	1.4044	80.88	66.42
33.75	1.3034	60.68	47.95	42.00	1.4078	81.56	67.18
34.00	1.3063	61.26	48.42	42.25	1.4112	82.24	67.95
34.25	1.3093	61.86	48.90	42.50	1.4146	82.92	68.73
34.50	1.3122	62.44	49.35	42.75	1.4181	83.62	69.52
34.75	1.3152	63.04	49.83	43.00	1.4216	84.32	70.33
35.00	1.3182	63.64	50.32	43.25	1.4251	85.02	71.15
35.25	1.3212	64.24	50.81	43.50	1.4286	85.72	71.98
35.50	1.3242	64.84	51.30	43.75	1.4321	86.42	72.82
35.75	1.3273	65.46	51.80	44.00	1.4356	87.12	73.67
36.00	1.3303	66.06	52.30	44.25	1.4392	87.84	74.53
36.25	1.3334	66.68	52.81	44.50	1.4428	88.56	75.40
36.50	1.3364	67.28	53.32	44.75	1.4464	89.28	76.28
36.75	1.3395	67.90	53.84	45.00	1.4500	90.00	77.17
37.00	1.3426	68.52	54.36	45.25	1.4536	90.72	78.07
37.25	1.3457	69.14	54.89	45.50	1.4573	91.46	79.03
37.50	1.3488	69.76	55.43	45.75	1.4610	92.20	80.04
37.75	1.3520	70.40	55.97	46.00	1.4646	92.92	81.08
38.00	1.3551	71.02	56.52	46.25	1.4684	93.68	82.18
38.25	1.3583	71.66	57.08	46.50	1.4721	94.42	83.33
38.50	1.3615	72.30	57.65	46.75	1.4758	95.16	84.48
38.75	1.3647	72.94	58.23	47.00	1.4796	95.92	85.70
39.00	1.3679	73.58	58.82	47.25	1.4834	96.68	86.98
39.25	1.3712	74.24	59.43	47.50	1.4872	97.44	88.32
39.50	1.3744	74.88	60.06	47.75	1.4910	98.20	89.76
39.75	1.3777	75.54	60.71	48.00	1.4948	98.96	91.35
40.00	1.3810	76.20	61.38	48.25	1.4987	99.74	93.13
40.25	1.3843	76.86	62.07	48.50	1.5026	100.52	95.11
40.50	1.3876	77.52	62.77				

Specific Gravity determinations were made at 60° F., compared with water at 60° F.
From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.}}.$$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.
Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

At 10° — 20° Bé. — 1/30° Bé. or .00029 Sp. Gr. = 1° F.
20° — 30° Bé. — 1/23° Bé. or .00044 " " = 1° F.
30° — 40° Bé. — 1/20° Bé. or .00060 " " = 1° F.
40° — 48.5° Bé. — 1/17° Bé. or .00084 " " = 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
New York, May 14, 1903. A. G. ROSENGARTEN, *Executive Committee*

VIII.—NITRIC ACID

LUNGE AND REY

Specific Gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.000	0.08	0.10	1	1	1.195	27.10	31.62	324	378
1.005	0.85	1.00	8	10	1.200	27.74	32.36	333	388
1.010	1.62	1.90	16	19	1.205	28.36	33.09	342	399
1.015	2.39	2.80	24	28	1.210	28.99	33.82	351	409
1.020	3.17	3.70	33	38	1.215	29.61	34.55	360	420
1.025	3.94	4.60	40	47	1.220	30.24	35.28	369	430
1.030	4.71	5.50	49	57	1.225	30.88	36.03	378	441
1.035	5.47	6.38	57	66	1.230	31.53	36.78	387	452
1.040	6.22	7.26	64	75	1.235	32.17	37.53	397	463
1.045	6.97	8.13	73	85	1.240	32.82	38.29	407	475
1.050	7.71	8.99	81	94	1.245	33.47	39.05	417	486
1.055	8.43	9.84	89	104	1.250	34.13	39.82	427	498
1.060	9.15	10.68	97	113	1.255	34.78	40.58	437	509
1.065	9.87	11.51	105	123	1.260	35.44	41.34	447	521
1.070	10.57	12.33	113	132	1.265	36.09	42.10	457	533
1.075	11.27	13.15	121	141	1.270	36.75	42.87	467	544
1.080	11.96	13.95	129	151	1.275	37.41	43.64	477	556
1.085	12.64	14.74	137	160	1.280	38.07	44.41	487	568
1.090	13.31	15.53	145	169	1.285	38.73	45.18	498	581
1.095	13.99	16.32	153	179	1.290	39.39	45.95	508	593
1.100	14.67	17.11	161	188	1.295	40.05	46.72	519	605
1.105	15.34	17.89	170	198	1.300	40.71	47.49	529	617
1.110	16.00	18.67	177	207	1.305	41.37	48.26	540	630
1.115	16.67	19.45	186	217	1.310	42.06	49.07	551	643
1.120	17.34	20.23	195	227	1.315	42.76	49.89	562	656
1.125	18.00	21.00	202	236	1.320	43.47	50.71	573	669
1.130	18.66	21.77	211	246	1.325	44.17	51.53	585	683
1.135	19.32	22.54	219	256	1.330	44.89	52.37	597	697
1.140	19.98	23.31	228	266	1.3325	45.26	52.80	603	704
1.145	20.64	24.08	237	276	1.335	45.62	53.22	609	710
1.150	21.29	24.84	245	286	1.340	46.35	54.07	621	725
1.155	21.94	25.60	254	296	1.345	47.08	54.93	633	739
1.160	22.60	26.36	262	306	1.350	47.82	55.79	645	753
1.165	23.25	27.12	271	316	1.355	48.57	56.66	658	768
1.170	23.90	27.88	279	326	1.360	49.35	57.57	671	783
1.175	24.54	28.63	288	336	1.365	50.13	58.48	684	798
1.180	25.18	29.38	297	347	1.370	50.91	59.39	698	814
1.185	25.83	30.13	306	357	1.375	51.69	60.30	711	829
1.190	26.47	30.88	315	367	1.380	52.52	61.27	725	846

VIII.—NITRIC ACID (Continued)

Specific Gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.3833	53.08	61.92	735	857	1.495	78.52	91.60	1174	1369
1.385	53.35	62.24	739	862	1.500	80.65	94.09	1210	1411
1.390	54.20	63.23	753	879	1.501	81.09	94.60	1217	1420
1.395	55.07	64.25	768	896	1.502	81.50	95.08	1224	1428
1.400	55.97	65.30	783	914	1.503	81.91	95.55	1231	1436
1.405	56.92	66.40	800	933	1.504	82.29	96.00	1238	1444
1.410	57.86	67.50	816	952	1.505	82.63	96.39	1244	1451
1.415	58.83	68.63	832	971	1.506	82.94	96.76	1249	1457
1.420	59.83	69.80	849	991	1.507	83.26	97.13	1255	1464
1.425	60.84	70.98	867	1011	1.508	83.58	97.50	1260	1470
1.430	61.86	72.17	885	1032	1.509	83.87	97.84	1265	1476
1.435	62.91	73.39	903	1053	1.510	84.09	98.10	1270	1481
1.440	64.01	74.68	921	1075	1.511	84.28	98.32	1274	1486
1.445	65.13	75.98	941	1098	1.512	84.46	98.53	1277	1490
1.450	66.24	77.28	961	1121	1.513	84.63	98.73	1280	1494
1.455	67.38	78.60	981	1144	1.514	84.78	98.90	1283	1497
1.460	68.56	79.98	1001	1168	1.515	84.92	99.07	1287	1501
1.465	69.79	81.42	1023	1193	1.516	85.04	99.21	1289	1504
1.470	71.06	82.90	1045	1219	1.517	85.15	99.34	1292	1507
1.475	72.39	84.45	1068	1246	1.518	85.26	99.46	1294	1510
1.480	73.76	86.05	1092	1274	1.519	85.35	99.57	1296	1512
1.485	75.18	87.70	1116	1302	1.520	85.44	99.67	1299	1515
1.490	76.80	89.60	1144	1335					

IX.—SULPHURIC ACID

By W. C. Ferguson and H. P. Talbot

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.*	Pounds O. V. in 1 Cubic Foot.
0	1.0000	0.0	0.00	62.37	0.00	0.00
1	1.0069	1.4	1.02	62.80	1.09	0.68
2	1.0140	2.8	2.08	63.24	2.23	1.41
3	1.0211	4.2	3.13	63.69	3.36	2.14
4	1.0284	5.7	4.21	64.14	4.52	2.90
5	1.0357	7.1	5.28	64.60	5.67	3.66
6	1.0432	8.6	6.37	65.06	6.84	4.45
7	1.0507	10.1	7.45	65.53	7.99	5.24
8	1.0584	11.7	8.55	66.01	9.17	6.06
9	1.0662	13.2	9.66	66.50	10.37	6.89
10	1.0741	14.8	10.77	66.99	11.56	7.74
11	1.0821	16.4	11.89	67.49	12.76	8.61
12	1.0902	18.0	13.01	68.00	13.96	9.49
13	1.0985	19.7	14.13	68.51	15.16	10.39
14	1.1069	21.4	15.25	69.04	16.36	11.30
15	1.1154	23.1	16.38	69.57	17.58	12.23
16	1.1240	24.8	17.53	70.10	18.81	13.19
17	1.1328	26.6	18.71	70.65	20.08	14.18
18	1.1417	28.3	19.89	71.21	21.34	15.20
19	1.1508	30.2	21.07	71.78	22.61	16.23
20	1.1600	32.0	22.25	72.35	23.87	17.27
21	1.1694	33.9	23.43	72.94	25.14	18.34
22	1.1789	35.8	24.61	73.53	26.41	19.42
23	1.1885	37.7	25.81	74.13	27.69	20.53
24	1.1983	39.7	27.03	74.74	29.00	21.68

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Sp. Grs., the corresponding degrees Baumé were calculated by the following formula: Baumé $= 145 - 145/\text{Sp. Gr.}$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

* 66° Baumé = Sp. Gr. 1.8354 = Oil of Vitriol (O. V.).

1 cu. ft. water at 60° F. weighs 62.37 lbs. av.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

H_2SO_4 = 100 per cent.

	% H_2SO_4	% O. V.	%60°
O. V.	= 93.19	= 100.00	= 119.98
60°	= 77.67	= 83.35	= 100.00
50°	= 62.18	= 66.72	= 80.06

IX.—SULPHURIC ACID (Continued)

Degrees Baumé.	* Freezing (Melting) Point. F.
0	32.0
1	31.2
2	30.5
3	29.8
4	28.9
5	28.1
6	27.2
7	26.3
8	25.1
9	24.0
10	22.8
11	21.5
12	20.0
13	18.3
14	16.6
15	14.7
16	12.6
17	10.2
18	7.7
19	4.8
20	+ 1.6
21	− 1.8
22	− 6.0
23	−11
24	−16

APPROXIMATE BOILING POINTS

50° B,	295° F.
60° "	386° "
61° "	400° "
62° "	415° "
63° "	432° "
64° "	451° "
65° "	485° "
66° "	538° "

FIXED POINTS

Specific Gravity.	Per Cent H_2SO_4.	Specific Gravity.	Per Cent H_2SO_4.
1.0000	.00	1.5281	62.34
1.0048	.71	1.5440	63.79
1.0347	5.14	1.5748	66.51
1.0649	9.48	1.6272	71.00
1.0992	14.22	1.6679	74.46
1.1353	19.04	1.7044	77.54
1.1736	23.94	1.7258	79.40
1.2105	28.55	1.7472	81.32
1.2513	33.49	1.7700	83.47
1.2951	38.64	1.7959	86.36
1.3441	44.15	1.8117	88.53
1.3947	49.52	1.8194	89.75
1.4307	53.17	1.8275	91.32
1.4667	56.68	1.8354	93.19
1.4822	58.14		

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, Jour. of Lon. Ch. Soc., vol. 57, p. 363.

AUTHORITIES — W. C. FERGUSON; H. P. TALBOT.

This table has been approved and adopted as a standard by the Manufacturing Chemists' Association of the United States.

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ARTHUR WYMAN,
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Executive Committee

New York, June 23, 1904.

IX.—SULPHURIC ACID (Continued)

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
25	1.2083	41.7	28.28	75.36	30.34	22.87
26	1.2185	43.7	29.53	76.00	31.69	24.08
27	1.2288	45.8	30.79	76.64	33.04	25.32
28	1.2393	47.9	32.05	77.30	34.39	26.58
29	1.2500	50.0	33.33	77.96	35.76	27.88
30	1.2609	52.2	34.63	78.64	37.16	29.22
31	1.2719	54.4	35.93	79.33	38.55	30.58
32	1.2832	56.6	37.26	80.03	39.98	32.00
33	1.2946	58.9	38.58	80.74	41.40	33.42
34	1.3063	61.3	39.92	81.47	42.83	34.90
35	1.3182	63.6	41.27	82.22	44.28	36.41
36	1.3303	66.1	42.63	82.97	45.74	37.95
37	1.3426	68.5	43.99	83.74	47.20	39.53
38	1.3551	71.0	45.35	84.52	48.66	41.13
39	1.3679	73.6	46.72	85.32	50.13	42.77
40	1.3810	76.2	48.10	86.13	51.61	44.45
41	1.3942	78.8	49.47	86.96	53.08	46.16
42	1.4078	81.6	50.87	87.80	54.58	47.92
43	1.4216	84.3	52.26	88.67	56.07	49.72
44	1.4356	87.1	53.66	89.54	57.58	51.56
45	1.4500	90.0	55.07	90.44	59.09	53.44
46	1.4646	92.9	56.48	91.35	60.60	55.36
47	1.4796	95.9	57.90	92.28	62.13	57.33
48	1.4948	99.0	59.32	93.23	63.65	59.34
49	1.5104	102.1	60.75	94.20	65.18	61.40
50	1.5263	105.3	62.18	95.20	66.72	63.52
51	1.5426	108.5	63.66	96.21	68.31	65.72
52	1.5591	111.8	65.13	97.24	69.89	67.96
53	1.5761	115.2	66.63	98.30	71.50	70.28
54	1.5934	118.7	68.13	99.38	73.11	72.66
55	1.6111	122.2	69.65	100.48	74.74	75.10
56	1.6292	125.8	71.17	101.61	76.37	77.60
57	1.6477	129.5	72.75	102.77	78.07	80.23
58	1.6667	133.3	74.36	103.95	79.79	82.95
59	1.6860	137.2	75.99	105.16	81.54	85.75

IX.—SULPHURIC ACID (Continued)

Degrees Baumé.	* Freezing (Melting) Point. °F.	Per Cent 60° Baumé.	Pounds 60° Baumé in 1 Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in 1 Cubic Foot.
25	−23				
26	−30				
27	−39				
28	−49				
29	−61				
30	−74				
31	−82				
32	−96				
33	−97				
34	−91				
35	−81				
36	−70				
37	−60				
38	−53				
39	−47				
40	−41	61.93	53.34	77.36	66.63
41	−35	63.69	55.39	79.56	69.19
42	−31	65.50	57.50	81.81	71.83
43	−27	67.28	59.66	84.05	74.53
44	−23	69.09	61.86	86.30	77.27
45	−20	70.90	64.12	88.56	80.10
46	−14	72.72	66.43	90.83	82.98
47	−15	74.55	68.79	93.12	85.93
48	−18	76.37	71.20	95.40	88.94
49	−22	78.22	73.68	97.70	92.03
50	−27	80.06	76.21	100.00	95.20
51	−33	81.96	78.85	102.38	98.50
52	−39	83.86	81.54	104.74	101.85
53	−49	85.79	84.33	107.15	105.33
54	−59	87.72	87.17	109.57	108.89
55	.. (Below 40)	89.67	90.10	112.01	112.55
56	.. (Below 40)	91.63	93.11	114.46	116.30
57	.. (Below 40)	93.67	96.26	117.00	120.24
58	.. (Below 40)	95.74	99.52	119.59	124.31
59	− 7 (Below 40)	97.84	102.89	122.21	128.52

ALLOWANCE FOR TEMPERATURE

At 10°	Bé.	.029°	Bé. or	.00023	Sp. Gr.	= 1° F.
" 20°	"	.036°	"	.00034	"	= 1° "
" 30°	"	.035°	"	.00039	"	= 1° "
" 40°	"	.031°	"	.00041	"	= 1° "
" 50°	"	.028°	"	.00045	"	= 1° "
" 60°	"	.026°	"	.00053	"	= 1° "
" 63°	"	.026°	"	.00057	"	= 1° "
" 66°	"	.0235°	"	.00054	"	= 1° "

IX.—SULPHURIC ACID (Continued)

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
60	1.7059	141.2	77.67	106.40	83.35	88.68
61	1.7262	145.2	79.43	107.66	85.23	91.76
62	1.7470	149.4	81.30	108.96	87.24	95.06
63	1.7683	153.7	83.34	110.29	89.43	98.63
64	1.7901	158.0	85.66	111.65	91.92	102.63
64¼	1.7957	159.1	86.33	112.00	92.64	103.75
64½	1.8012	160.2	87.04	112.34	93.40	104.93
64¾	1.8068	161.4	87.81	112.69	94.23	106.19
65	1.8125	162.5	88.65	113.05	95.13	107.54
65¼	1.8182	163.6	89.55	113.40	96.10	108.97
65½	1.8239	164.8	90.60	113.76	97.22	110.60
65¾	1.8297	165.9	91.80	114.12	98.51	112.42
66	1.8354	167.1	93.19	114.47	100.00	114.47

X.—SULPHURIC ACID TABLE

94–100% H_2SO_4

By H. B. Bishop

The acid used in this table was prepared from Baker and Adamson's c.p. sulphuric acid 95 per cent, which was strengthened to 100 per cent by the addition of fuming sulphuric acid made by distilling fuming acid (70 per cent free SO_3) into a portion of the 95 per cent c.p. acid. The final acid was tested for impurities: residue upon evaporation, chlorine, niter and sulphur dioxide. The only impurity found was a trace of sulphur dioxide (0.001 per cent) which was less than the sensitiveness of the determination.

The analytical and specific gravity determinations, and the allowance for temperature were made in the same manner, and with the same accuracy as in the sulphuric acid table adopted in 1904, the specific gravity 1.8354 and 93.19 per cent H_2SO_4 being taken as a standard.

The actual determinations were made within a few hundredths of a per cent of the points given in the table, the even percentages being calculated by interpolation.

Bé.	Sp. Gr. at 60° F.	Per Cent. H_2SO_4	Wt. 1 Cu. Ft.	Allowance for Temperature.
66	1.8354	93.19	114.47	At 94% .00054 sp.gr. = 1° F.
66.12	1.8381	94.00	114.64	" 96 .0053 " = 1° F.
66.23	1.8407	95.00	114.80	" 97.5 .00052 " = 1° F.
66.31	1.8427	96.00	114.93	" 100 .00052 " = 1° F.
66.36	1.8437	97.00	114.99	
66.36	1.8439	97.50	114.99	
66.36	1.8437	98.00	114.99	
66.30	1.8424	99.00	114.91	
66.16	1.8391	100.00	114.70	

XI.—MELTING-POINTS OF ACETIC ACID

RUDORFF, Ber. 3, 390.

100 gr. $H.C_2H_3O_2$ mixed with gr. water.	100 parts by weight contain parts water.	Melting (solidifying) point °C.	100 gr. $H.C_2H_3O_2$ mixed with gr. water.	100 parts by weight contain parts water.	Melting (solidifying) point °C.
0.0	0.0	16.7°	8.0	7.407	6.25°
0.5	0.497	15.65	9.0	8.257	5.3
1.0	0.990	14.8	10.0	9.090	4.3
1.5	1.477	14.0	11.0	9.910	3.6
2.0	1.961	13.25	12.0	10.774	2.7
3.0	2.912	11.95	15.0	13.043	−0.2
4.0	3.846	10.5	18.0	15.324	−2.6
5.0	4.761	9.4	21.0	17.355	−5.1
6.0	5.660	8.2	24.0	19.354	−7.4
7.0	6.542	7.1			

Boiling point 100% acid 117 8°.

XII.—ACETIC ACID AT 15°

OUDEMANS

Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

XIII.—PHOSPHORIC ACID AT 17.5°

Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15.84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

XIV.—AQUA AMMONIA

ACCORDING TO W. C. FERGUSON

Degrees Baumé.	Sp. Gr. 60°/60° F.	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. 60°/60° F.	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. 60°/60° F.	Per Cent NH_3.
10.00	1.0000	.00	16.50	.9556	11.18	23.00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9929	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	25.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	.8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9226	21.12	28.25	.8847	33.81
15.50	.9622	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34.79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

Specific Gravity determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = \frac{140}{\text{Sp. Gr.}} - 130.$$

* Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should *always* be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

XIV.—AQUA AMMONIA (Continued)

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

Corrections to be Added for Each Degree Below 60° F.			Corrections to be Subtracted for Each Degree Above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° Bé	.015° Bé	.017° Bé	.020° Bé	.022° Bé	.024° Bé	.026° Bé
16°	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18°	.027 "	.029 "	.031 "	.033 "	.035 "	.037 "
20°	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22°	.039 "	.042 "	.043 "	.045 "	.047 "	
26°	.053 "	.057 "	.057 "	.059 "		

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER,
HENRY HOWARD,
JAS. L. MORGAN,
ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee.

New York, May 14, 1903.

XV.—SODIUM-HYDROXIDE SOLUTION AT 15°

LUNGE

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Per Cent Na_2O.	Per Cent NaOH.	1 Liter contains Grams	
					Na_2O.	NaOH.
1.007	1.0	1.4	0.47	0.61	4	6
1.014	2.0	2.8	0.93	1.20	9	12
1.022	3.1	4.4	1.55	2.00	16	21
1.029	4.1	5.8	2.10	2.70	22	28
1.036	5.1	7.2	2.60	3.35	27	35
1.045	6.2	9.0	3.10	4.00	32	42
1.052	7.2	10.4	3.60	4.64	38	49
1.060	8.2	12.0	4.10	5.29	43	56
1.067	9.1	13.4	4.55	5.87	49	63
1.075	10.1	15.0	5.08	6.55	55	70
1.083	11.1	16.6	5.67	7.31	61	79
1.091	12.1	18.2	6.20	8.00	68	87
1.100	13.2	20.0	6.73	8.68	74	95
1.108	14.1	21.6	7.30	9.42	81	104
1.116	15.1	23.2	7.80	10.06	87	112
1.125	16.1	25.0	8.50	10.97	96	123
1.134	17.1	26.8	9.18	11.84	104	134
1.142	18.0	28.4	9.80	12.64	112	144
1.152	19.1	30.4	10.50	13.55	121	156
1.162	20.2	32.4	11.14	14.37	129	167
1.171	21.2	34.2	11.73	15.13	137	177
1.180	22.1	36.0	12.33	15.91	146	183
1.190	23.1	38.0	13.00	16.77	155	200
1.200	24.2	40.0	13.70	17.67	164	212
1.210	25.2	42.0	14.40	18.58	174	225
1.220	26.1	44.0	15.18	19.58	185	239
1.231	27.2	46.2	15.96	20.59	196	253
1.241	28.2	48.2	16.76	21.42	208	266
1.252	29.2	50.4	17.55	22.64	220	283
1.263	30.2	52.6	18.35	23.67	232	299
1.274	31.2	54.8	19.23	24.81	245	316
1.285	32.2	57.0	20.00	25.80	257	332
1.297	33.2	59.4	20.80	26.83	270	348
1.308	34.1	61.6	21.55	27.80	282	364
1.320	35.2	64.0	22.35	28.83	295	381
1.332	36.1	66.4	23.20	29.93	309	399
1.345	37.2	69.0	24.20	31.22	326	420

XV.—SODIUM HYDROXIDE SOLUTION AT 15° (Continued)

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Per Cent Na_2O.	Per Cent NaOH.	1 Liter contains Grams	
					Na_2O.	NaOH.
1.357	38.1	71.4	25.17	32.47	342	441
1.370	39.2	74.0	26.12	33.69	359	462
1.383	40.2	76.6	27.10	34.96	375	483
1.397	41.2	79.4	28.10	36.25	392	506
1.410	42.2	82.0	29.05	37.47	410	528
1.424	43.2	84.8	30.08	38.80	428	553
1.438	44.2	87.6	31.00	39.99	446	575
1.453	45.2	90.6	32.10	41.41	466	602
1.468	46.2	93.6	33.20	42.83	487	629
1.483	47.2	96.6	34.40	44.38	510	658
1.498	48.2	99.6	35.70	46.15	535	691
1.514	49.2	102.8	36.90	47.60	559	721
1.530	50.2	106.0	38.00	49.02	581	750

XVI.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERC −2° TO +36° C.

ACCORDING TO REGNAULT, BROCH, AND WEIBE

°C.	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
−2	3.958	3.929	3.900	3.872	3.844	3.815	3.787	3.760	3.732	3.705
−1	4.258	4.227	4.197	4.166	4.136	4.106	4.076	4.046	4.016	3.987
−0	4.579	4.546	4.513	4.481	4.448	4.416	4.384	4.352	4.321	4.289
0	4.579	4.612	4.646	4.679	4.713	4.747	4.782	4.816	4.851	4.886
1	4.921	4.957	4.992	5.028	5.064	5.101	5.137	5.174	5.211	5.248
2	5.286	5.324	5.362	5.400	5.438	5.477	5.516	5.555	5.595	5.635
3	5.675	5.715	5.755	5.796	5.837	5.878	5.920	5.961	6.003	6.046
4	6.088	6.131	6.174	6.217	6.261	6.305	6.349	6.393	6.438	6.483
5	6.528	6.574	6.620	6.666	6.712	6.759	6.806	6.853	6.901	6.949
6	6.997	7.045	7.094	7.143	7.192	7.242	7.292	7.342	7.392	7.443
7	7.494	7.546	7.598	7.650	7.702	7.755	7.808	7.861	7.914	7.968
8	8.023	8.077	8.132	8.187	8.243	8.299	8.355	8.412	8.469	8.526
9	8.584	8.642	8.700	8.759	8.818	8.877	8.937	8.997	9.057	9.118
10	9.179	9.240	9.302	9.364	9.427	9.490	9.553	9.616	9.680	9.745
11	9.810	9.875	9.940	10.006	10.072	10.139	10.206	10.274	10.342	10.410
12	10.479	10.548	10.617	10.687	10.757	10.828	10.899	10.970	11.042	11.114
13	11.187	11.260	11.333	11.407	11.481	11.556	11.631	11.706	11.782	11.859
14	11.936	12.013	12.091	12.169	12.247	12.326	12.406	12.486	12.566	12.647
15	12.728	12.810	12.892	12.974	13.057	13.141	13.225	13.309	13.394	13.480
16	13.565	13.651	13.738	13.825	13.913	14.001	14.090	14.179	14.269	14.359
17	14.450	14.541	14.632	14.724	14.817	14.910	15.003	15.097	15.192	15.287
18	15.383	15.479	15.575	15.672	15.770	15.868	15.967	16.066	16.166	16.266
19	16.367	16.469	16.571	16.673	16.776	16.880	16.984	17.088	17.193	17.299
20	17.406	17.513	17.620	17.728	17.837	17.947	18.057	18.167	18.278	18.390
21	18.503	18.616	18.729	18.844	18.959	19.074	19.190	19.307	19.424	19.542
22	19.661	19.780	19.900	20.021	20.142	20.264	20.386	20.510	20.634	20.758
23	20.883	21.010	21.137	21.264	21.393	21.522	21.652	21.782	21.913	22.045
24	22.178	22.311	22.446	22.581	22.716	22.853	22.990	23.128	23.266	23.406
25	23.546	23.686	23.828	23.970	24.113	24.257	24.401	24.547	24.693	24.839
26	24.987	25.135	25.284	25.434	25.584	25.736	25.888	26.041	26.195	26.349
27	26.505	26.661	26.818	26.976	27.134	27.294	27.454	27.615	27.777	27.939
28	28.103	28.267	28.432	28.599	28.766	28.933	29.102	29.271	29.442	29.613
29	29.785	29.958	30.132	30.307	30.482	30.659	30.836	31.015	31.194	31.374
30	31.555	31.737	31.919	32.103	32.288	32.473	32.660	32.847	33.036	33.225
31	33.416	33.607	33.799	33.992	34.187	34.382	34.578	34.775	34.973	35.172
32	35.372	35.573	35.775	35.978	36.182	36.387	36.593	36.800	37.008	37.217
33	37.427	37.638	37.851	38.064	38.278	38.493	38.710	38.927	39.146	39.365
34	39.586	39.807	40.030	40.254	40.479	40.705	40.933	41.161	41.390	41.621
35	41.583	42.085	42.319	42.554	42.791	43.028	43.266	43.506	43.747	43.989

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS *

Substance.	Formula.	Molecular or Atomic Weight.	Normal Coefficient 1 c.c. = gm.	Solubility in 100 Gms. Water.	Indicator.
Acetic acid	$HC_2H_3O_2$	60.03	.06003		
Aluminium	Al	27.10	.009033		
chloride	Al_2Cl_6	266.96	.04449	$69.87^{15°}$	P.
chloride	$Al_2Cl_6 \cdot 12H_2O$	483.15	.08053	40	P.
oxide	Al_2O_3	102.20	.01703	insol.	
sulphate	$Al_2(SO_4)_3$	342.38	.05706	$36.1^{20°}$	P.
sulphate	$Al_2(SO_4)_318H_2O$	666.67	.11111	87	P.
Ammonia	NH_3	17.03	.01703	.....	M.
Ammonium	NH_4	18.04	.01804	.....	M.
chloride	NH_4Cl	53.50	.05350	$29.4^{0°}$	M.
hydroxide	NH_4OH	35.05	.03505	.....	M.
nitrate	NH_4NO_3	80.05	.08005	$118^{0°}$	M.
sulphate	$(NH_4)_2SO_4$	132.14	.06607	$71^{0°}$	M.
Antimony	Sb	120.20	.06010		
Arsenic	As	74.96	.03748		
oxide	As_2O_5	229.92	.03832 [1]	150	
Arsenous oxide	As_2O_3	197.92	.03299	$1.7^{16°}$	
Arsenious oxide	As_2O_3	197.92	.04948 [3]	$1.7^{16°}$	
Barium	Ba	137.37	.068685		
carbonate	$BaCO_3$	197.37	.098685	$.0022^{20°}$	M.
chloride	$BaCl_2$	208.29	.104145	$30.9^{0°}$	
chloride	$BaCl_22H_2O$	244.32	.12216	$36.2^{0°}$	
hydroxide	$Ba(OH)_2$	171.38	.08569		
hydroxide	$Ba(OH)_28H_2O$	315.51	.15775	$5.56^{15°}$	
sulphate	$BaSO_4$	233.44	.11672	$.000172^{0°}$	
oxide	BaO	153.37	.076685	$1.5^{0°}$	
peroxide	BaO_2	169.37	.08469	insol.	
Bromine	Br	79.92	.07992	$4.17^{0°}$	
Cadmium carbonate	$CdCO_3$	172.40	.08620	insol.	
chloride	$CdCl_2$	183.32	.09166	$140^{20°}$	
chloride	$CdCl_22H_2O$	219.35	.109675	$168^{20°}$	
sulphide	CdS	144.47	.072235	insol.	
Calcium	Ca	40.00	.020035		
carbonate	$CaCO_3$	100.07	.050035	.0013	M.
chloride	$CaCl_2$	110.99	.055495	$59.5^{0°}$	
chloride	$CaCl_26H_2O$	219.086	.109543	$117.4^{0°}$	
hydroxide	$Ca(OH)_2$	74.09	.037045	$.17^{0°}$	
oxide	CaO	56.07	.028035	$.13^{0°}$	
sulphate	$CaSO_4$	136.14	.06807	$.179^{0°}$	
sulphide	CaS	72.14	.03607	$.15^{10°}$	
Carbon	C	12.005	.003002	insol.	
dioxide	CO_2	44.005	.022003 [1]	179.67 cc.$^{0°}$	
dioxide	CO_2	44.005	.044005 [2]	"	P.
Chlorine	Cl	35.46	.03546	150 cc.$^{0°}$	
Chromic anhydride	CrO_3	100.00	.033333 [3]	$163.4^{0°}$	
oxide	Cr_2O_3	152.00	.025333 [3]	insol.	
Citric acid	$H_3C_6H_5O_7$	192.06	.06402	133.	
Cobalt	Co	58.97	.029485		
Copper	Cu	63.57	.031785		
oxide	CuO	79.57	.07957		
sulphate	$CuSO_4$	159.63	.15963	$20^{0°}$	
sulphate	$CuSO_45H_2O$	249.71	.24971	$31.61^{0°}$	
sulphide	CuS	95.63	.047815	.000033	

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

* Compiled and arranged by R. M. Meiklejohn.

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (Continued)

Substance.	Formula.	Molecular or Atomic Weight.	Normal Coefficient 1 c.c. = gm.	Solubility in 100 Gms. Water.	Indicator.
Cyanogen	CN	26.005	.026005		
Ferric oxide	Fe_2O_3	159.68	.07984 [3]		
Ferrous oxide	FeO	71.84	.07184 [3]	insol.	
sulphate	$FeSO_4$	151.90	.15190 [3]		
sulphate	$FeSO_47H_2O$	278.01	.27801 [3]	32.8°	
ammon'm sulphate	$FeSO_4(NH_4)_2SO_46H_2O$	392.14	.39214	18°	
Hydrobromic acid	HBr	80.928	.08093	221.2°	
Hydrochloric acid	HCl	36.47	.03647	82.5[10]°	
Hydrocyanic acid	HCN	27.02	.02702		
Hydrofluoric acid	HF	20.01	.02001	264	
Hydroiodic acid	HI	127.93	.12793		
Hydrogen peroxide	H_2O_2	34.016	.017008		
Hydrogen sulphide	H_2S	34.076	.017038	437 cc.°	
Iodine	I	126.92	.12692	.0182[11]°	
Iron	Fe	55.84	.05584		
Lead	Pb	207.20	.10360		
carbonate	$PbCO_3$	267.20	.13360	.00198	M.
chromate	$PbCrO_4$	323.20	.16160	.00002[18]°	
oxide	PbO	223.20	.11160		
peroxide	PbO_2	239.20	.11960		
sulphide	PbS	239.26	.11963	.0001	
Magnesium	Mg	24.32	.01216		
carbonate	$MgCO_3$	84.32	.04216	.0106	M.
chloride	$MgCl_2$	95.24	.04762	52.2°	M.
chloride	$MgCl_26H_2O$	203.34	.10167	167	M.
oxide	MgO	40.32	.02016	.00062	M.
sulphate	$MgSO_4$	120.38	.06019	26.9°	M.
sulphate	$MgSO_47H_2O$	246.49	.123245	76.9°	M.
Malic acid	$H_2C_4H_4O_5$	134.06	.06703		
Manganese	Mn	54.93	.027465		
chloride	$MnCl_2$	125.85	.062925	62.16[10]°	
peroxide	MnO_2	86.93	.043465	insol.	
sulphate	$MnSO_4$	150.99	.075495	53.2°	
Mercuric chloride	$HgCl_2$	271.52	.13576	5.73°	
Nickel	Ni	58.68	.02934		
Nitric acid	HNO_3	63.02	.06302 [2]		
Nitric acid	HNO_3	63.02	.021006 [3]		
Nitrogen trioxide	N_2O_3	76.02	.019005 [3]		
pentoxide	N_2O_5	108.02	.05401 [2]		
pentoxide	N_2O_5	108.02	.018033 [3]		
Nitrous acid	HNO_2	47.02	.04702		
Nitrogen	N	14.01	.01401		
Oxalic acid	$H_2C_2O_4$	90.02	.04501		
Oxalic acid	$H_2C_2O_42H_2O$	126.05	.063025	4.9°	
Phosphoric acid	H_3PO_4	98.06	.09806 [2]	v. sol.	M.
Phosphoric acid	H_3PO_4	98.06	.04903 [2]	v. sol.	P.
Phosphoric acid	H_3PO_4	98.06	.03268	v. sol.	
Potassium	K	39.10	.03910		
bicarbonate	K_2CO_3	100.11	.10011	22.4°	M.
bitartrate	$KHC_4H_4O_6$	188.14	.18814	.37°	P.
bromide	KBr	119.02	.11902	53.48°	
carbonate	K_2CO_3	138.20	.06910	89.4°	
chlorate	$KClO_3$	122.56	.020427 [3]	3.3°	M.

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (Continued)

Substance.	Formula.	Molecular or Atomic Weight.	Normal Coefficient 1 c.c. = gm.	Solubility in 100 Gms. Water.	Indicator.
Potassium chloride	KCl	74.56	.07456	28.5°	
chromate	K_2CrO_4	194.20	.06473 [3]	61.5°	
cyanide	KCN	65.11	.06511 [1]	v. sol.	
dichromate	$K_2Cr_2O_7$	294.20	.14710 [2]	4.9°	P.
dichromate	$K_2Cr_2O_7$	294.20	.04903 [3]	4.9°	
ferrocyanide	$K_4Fe(CN)_6$	368.30	.36830		
ferrocyanide	$K_4Fe(CN)_6 3H_2O$	422.35	.42235	$27.8^{12°}$	
hydroxide	KOH	56.11	.05611	$107^{15°}$	
iodate	KIO_3	214.02	.03567 [1]	4.74°	
iodide	KI	166.03	.16603	126.1°	
nitrate	KNO_3	101.11	.033703	13.3°	
nitrite	KNO_2	85.11	.08511	$300^{15.5°}$	
oxide	K_2O	94.20	.04710	v. sol.	
permanganate	$KMnO_4$	158.03	.031606	2.83°	
sulphide	K_2S	110.26	.05513	sol.	
sulphocyanate	$KCNS$	97.18	.09718	177.2°	
tartrate	$K_2H_4C_4O_6$	226.23	.11312	sol.	
Silver	Ag	107.88	.10788		
nitrate	$AgNO_3$	169.89	.16989	122°	
Sodium	Na	23.00	.02300		
bromide	$NaBr$	102.92	.10292	79.5°	
bicarbonate	$NaHCO_3$	84.01	.08401	6.90°	M.
carbonate	Na_2CO_3	106.00	.05300	7.1°	M.
chloride	$NaCl$	58.46	.05846	35.7°	
cyanide	$NaCN$	49.01	.04901	sol.	
hydroxide	$NaOH$	40.01	.04001	$133.3^{18°}$	
iodide	NaI	149.92	.14992 [1]	158.7°	
nitrate	$NaNO_3$	85.01	.02834	72.9°	
nitrite	$NaNO_2$	69.01	.06901	$83.3^{20°}$	
oxalate	$Na_2C_2O_4$	134.00	.06700	$3.22^{15.5°}$	
oxide	Na_2O	62.00	.03100	decomp.	
phosphate (mono)	NaH_2PO_4	120.06 [2]	.12006	v. sol.	M.
phosphate (disod)	Na_2HPO_4	142.05 [2]	.14205	.....	P.
phosphate (disod)	$Na_2HPO_4 12H_2O$	358.24 [2]	.35824	6.3°	P.
phosphate (trisod)	Na_3PO_4	164.04 [2]	.16404	.....	M.
sulphide	Na_2S	78.06	.03903	$15.4^{10°}$	
thiosulphate	$Na_2S_2O_3 5H_2O$	248.20	.24820	74.7°	
Stannous chloride	$SnCl_2$	189.62	.09481	83.9°	
chloride	$SnCl_2 2H_2O$	225.65	.112825	118.7°	
oxide	SnO	134.70	.06735	insol.	
Sulphur dioxide	SO_2	64.06	.03203	7979 cc.°	
trioxide	SO_3	80.06	.04003		
Sulphuric acid	H_2SO_4	98.076	.049038		
Tartaric acid	$H_2C_4H_4O_6$	150.05	.075025	115°	
Tin	Sn	118.70	.05935		
Zinc	Zn	65.37	.037685		
carbonate	$ZnCO_3$	125.37	.062685	$.001^{15°}$	
chloride	$ZnCl_2$	136.29	.068145	209°	
oxide	ZnO	81.37	.040685	.001	
sulphate	$ZnSO_4$	161.43	.080715	43.02°	
sulphate	$ZnSO_4 7H_2O$	287.54	.14377	115.2°	
sulphide	ZnS	97.43	.048715	.00069	

[1] Precipitation reagents. [2] Acids and bases. [3] Oxidising and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp C.

XVIII.—CONVERSION FACTORS *

A	B	A′	B′	A	B	A′	
Ag	AgBr	1.7408	0.5744	$AlCl_3$	Cl	0.7970	1.2
Ag	AgCl	1.3287	0.7526	$AlCl_3$	H_2SO_4	1.1023	0.9
Ag	AgCN	1.2411	0.8057	AlF_3	CaF	1.3925	0.7
Ag	AgI	2.1765	0.4595	Al_2O_3	Al	0.5303	1.8
Ag	$AgNO_3$	1.5748	0.6350	Al_2O_3	$AlCl_3$	2.6121	0.3
Ag	Ag_2O	1.0742	0.9310	Al_2O_3	$Al_4P_2O_7$	2.2336	0.4
Ag	Ag_3PO_4	1.2935	0.7731	Al_2O_3	$Al_2P_2O_5$	2.3902	0.4
Ag	$Ag_4P_2O_7$	1.4030	0.7126	Al_2O_3	$Al_2(SO_4)_3$	3.3504	0.2
Ag	As	0.2316	4.3175	Al_2O_3	$Al_2(SO_4)_3 \cdot 18H_2O$	6.5235	0.1
Ag	Br	0.7408	1.3489				
Ag	HBr	0.7505	1.3324	Al_2O_3	FeO	2.1088	0.4
Ag	Cl	0.3287	3.0423	Al_2O_3	Fe_2O_3	1.5625	0.6
Ag	HCl	0.3380	2.9590	Al_2O_3	H_2SO_4	2.8792	0.3
Ag	HI	1.1859	0.8433	Al_2O_3	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	9.2863	0.1
Ag	I	1.1765	0.8500				
Ag	KBr	1.1033	0.9064	Al_2O_3	$Na_2Al_2O_4$	1.6067	0.6
Ag	KCl	0.6911	1.4469	Al_2O_3	$(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$	8.8742	0.1
Ag	$KClO_3$	1.1361	0.8802				
Ag	$KClO_4$	1.2844	0.7786	Al_2O_3	$(SO_3)_3$	2.3504	.04
Ag	KCN	0.6035	1.6568	$AlPO_4$	Al	0.2219	4.5
Ag	KI	1.5390	0.6498	$AlPO_4$	Al_2O_3	0.4185	2.3
Ag	NaBr	0.9562	1.0458	$AlPO_4$	P_2O_5	0.5815	1.7
Ag	NaCl	0.5419	1.8453	$Al_4P_2O_7$	P_2O_5	0.6224	1.6
Ag	NaI	1.3897	0.7196	$Al_2P_2O_5$	P_2O_5	0.5816	1.7
AgBr	Br	0.4256	2.3498	$Al_2(SO_4)_3$	$BaSO_4$	1.3635	0.7
AgBr	BrO_3	0.6811	1.4681	$Al_2(SO_4)_3$	H_2SO_4	0.8594	1.1
AgBr	HBr	0.4311	2.3195	$Al_2(SO_4)_3$	$NaHCO_3$	1.4721	0.6
AgBr	KBr	0.6337	1.5779	$Al_2(SO_4)_3$	SO_3	0.7015	1.4
AgBr	$KBrO_3$	0.8893	1.1244				
AgBr	NaBr	0.5480	1.8257	As	Ag	4.3175	0.2
AgCl	Ag	0.7526	1.3287	As	As_2O_3	1.3201	0.75
AgCl	$AgNO_3$	1.1852	0.8437	As	As_2O_5	1.5336	0.65
AgCl	Cl	0.2474	4.0423	As	As_2S_3	1.6417	0.60
AgCl	HCl	0.2545	3.9305	As	2I	3.3862	0.29
AgCl	KCl	0.5202	1.9225	As	Na_2HAsO_4	2.4809	0.40
AgCl	$KClO_3$	0.8550	1.1695	As_2O_3	As_2O_5	1.1616	0.86
AgCl	NaCl	0.4078	2.4519	As_2O_3	As_2S_3	1.2435	0.80
AgCl	NH_4Cl	0.3732	2.6793	As_2O_3	As_2S_5	1.5674	0.63
AgCN	KCN	0.4863	2.0564	As_2O_3	4I	2.5652	0.38
AgCN	HCN	0.2020	4.9500	As_2O_5	NaH_2AsO_4	1.4264	0.70
AgI	NH_4I	0.6175	1.6194	As_2O_5	Na_2HAsO_4	1.6177	0.61
AgI	HI	0.5448	1.8354	As_2O_5	4I	2.2081	0.45
AgI	I	0.5406	1.8500				
AgI	IO_3	0.7450	1.3423	Au	$AuCl_3$	1.5394	0.649
AgI	I_2O_5	0.8131	1.2298	Au	$HAuCl_4 \cdot 4H_2O$	2.0898	0.478
AgI	I_2O_7	0.7109	1.4067				
AgI	KI	0.7071	1.4143	Au	$KAu(CN)_4 \cdot H_2O$	1.8172	0.550
AgI	KIO_3	0.9115	1.0971				
AgI	NaI	0.6385	1.5661				
$AgNO_2$	HNO_2	0.3055	3.2729	Ba	$Ba(C_2H_3O_2)_2$	1.8594	0.537
$AgNO_3$	HNO_3	0.3709	2.6959	Ba	$BaCrO_4$	1.8457	0.542
$AgNO_3$	NaCl	0.3441	2.9061	Ba	$BaSO_4$	1.7010	0.588
$AgNO_3$	N_2O_3	0.2470	4.0487	$BaCl_2$	$BaSO_4$	1.1207	0.892

$A \times A' = B$ and $B \times B' = A$.

* Compiled and arranged by W. W. Scott and B. S. Clark.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
$BaCl_2$	H_2SO_4	0.4709	2.1236	$BaSO_4$	SO_3	0.3430	2.9155
$BaCO_3$	CO_2	0.2229	4.4857	$BaSO_4$	SO_4	0.4115	2.4301
C(in $BaCO_3$)	H_2SO_4	8.1740	0.1223	$BaSO_4$	ZnS	0.4174	2.3957
$BaCrO_4$	Ba	0.5420	1.8457	$BaSO_4$	$ZnSO_4 \cdot 7H_2O$	1.2318	0.8118
$BaCrO_4$	$BaSO_4$	0.9213	1.0854				
$BaCrO_4$	Cr	0.2055	4.8651	Be		See Gl.	
$BaCrO_4$	Cr_2O_3	0.3002	3.3308				
$BaCrO_4$	K_2CrO_4	0.7666	1.3046	Bi	Bi_2O_3	1.1154	0.8965
$BaCrO_4$	$K_2Cr_2O_7$	0.5807	1.7220	$BiAsO_4$	Bi	0.5994	1.6683
$Ba(OH)_2$	H_2SO_4	0.5723	1.7473	BiOCl	Bi	0.8017	1.2474
BaO_2	Ba	0.8208	1.2184	BiOCl	$Bi(NO_3)_3 \cdot 5H_2O$	1.8658	0.5359
$BaSiF_6$	Ba	0.4912	2.0359				
$BaSiF_6$	BaF_2	0.6271	1.5948	BiOCl	Bi_2O_3	0.8942	1.1184
$BaSiF_6$	BaO	0.5484	1.8235	BiOCl	$BiONO_3$	1.1024	0.9072
$BaSiF_6$	F	0.4076	2.4533	Bi_2O_3	Bi	0.8965	1.1154
$BaSiF_6$	HF	0.4292	2.3297	Bi_2O_3	$BiONO_3$	1.2328	0.8112
$BaSiF_6$	H_2SiF_6	0.5160	1.9379	Bi_2O_3	$Bi(NO_3)_3 \cdot 5H_2O$	2.0867	0.4792
$BaSiF_6$	SiF_4	0.3729	2.6814				
$BaSiF_6$	SiO_2	0.2156	4.6380	Bi_2S_3	Bi	0.8122	1.2313
$BaSO_4$	$Al_2(SO_4)_3$	0.7334	1.3635	Bi_2S_3	Bi_2O_3	0.9059	1.1039
$BaSO_4$	Ba	0.5885	1.7010				
$BaSO_4$	$BaCl_2$	0.8928	1.1207	B	KBF_4	11.464	0.0872
$BaSO_4$	$BaCl_2 \cdot 2H_2O$	1.0466	0.9554	B_2O_3	B	0.3143	3.1819
$BaSO_4$	$BaCO_3$	0.8455	1.1827	B_2O_3	KBF_4	3.6029	0.2775
$BaSO_4$	$BaCrO_4$	1.0854	0.9213	B_2O_3	H_3BO_3	1.7721	0.5643
$BaSO_4$	$Ba(NO_3)_2$	1.1197	0.8931	B_2O_3	$Na_2B_4O_7 \cdot 10H_2O$	5.4594	0.1832
$BaSO_4$	BaO	0.6571	1.5219				
$BaSO_4$	BaO_2	0.7256	1.3782	KBF_4	H_3BO_3	0.4919	2.0331
$BaSO_4$	$Ba_3(PO_4)_2$	0.8456	1.1826	KBF_4	$Na_2B_4O_7 \cdot 10H_2O$	0.7576	1.3199
$BaSO_4$	BaS	0.7258	1.3778				
$BaSO_4$	$CaSO_3$	0.5147	1.9429				
$BaSO_4$	$CaSO_4$	0.5832	1.7147	Br	Ag	1.3498	0.7408
$BaSO_4$	FeS	0.3766	2.6554	Br	AgBr	2.3498	0.4256
$BaSO_4$	H_2S	0.1460	6.8493	Br	HBr	1.0130	0.9877
$BaSO_4$	H_2SO_3	0.3517	2.8437	Br	O	0.1001	9.9913
$BaSO_4$	H_2SO_4	0.4202	2.3801	BrO_3	Ag	0.8433	1.1858
$BaSO_4$	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	0.0167	0.9839	BrO_3	AgBr	1.4681	0.6811
$BaSO_4$	$KHSO_4$	0.5834	1.7141	Ca	$CaCl_2$	2.7687	0.3612
$BaSO_4$	MgO	0.1727	5.7897	Ca	CaO	1.3993	0.7146
$BaSO_4$	$MgSO_4 \cdot 7H_2O$	1.0560	0.9469	Ca	Cl_2	1.7690	0.5653
$BaSO_4$	$MnSO_4$	0.6469	1.5458	$Ca(CH_3CO_2)_2$	CaO	0.3546	2.8200
$BaSO_4$	Na_2CO_3	0.4541	2.2022	$Ca(CH_3CO_2)_2$	CH_3CO_2H	0.7594	1.3169
$BaSO_4$	$NaHSO_3$	0.4458	2.2432	$Ca(CH_3CO_2)_2$	H_2SO_4	0.6203	1.6120
$BaSO_4$	Na_2O	0.2656	3.7651	$CaCl_2$	$CaCO_3$	0.9016	1.1091
$BaSO_4$	Na_2S	0.3344	2.9904	$CaCl_2$	CaO	0.5052	1.9795
$BaSO_4$	Na_2SO_3	0.5401	1.8515	$CaCl_2$	$CaSO_4$	1.2265	0.8153
$BaSO_4$	$Na_2S_2O_3$	0.3387	2.9524	$CaCl_2$	Cl_2	0.6390	1.5650
$BaSO_4$	Na_2SO_4	0.6086	1.6431	$CaCO_3$	Ca	0.4006	2.4966
$BaSO_4$	$Na_2SO_4 \cdot 10H_2O$	1.3804	0.7244	$CaCO_3$	$CaCl_2$	1.1091	0.9016
				$CaCO_3$	$Ca(HCO_3)_2$	1.6197	0.6174
$BaSO_4$	$(NH_4)_2SO_4$	0.5661	1.7665	$CaCO_3$	CaO	0.5603	1.7847
$BaSO_4$	$PbSO_4$	1.2987	0.7700	$CaCO_3$	CO_2	0.4397	2.2743
$BaSO_4$	S	0.1373	7.2812	$CaCO_3$	$CaSO_4$	1.3604	0.7351
$BaSO_4$	SO_2	0.2744	3.6443	$CaCO_3$	$CaSO_4 \cdot 2H_2O$	1.7204	0.5813

$A \times A' = B$ and $B \times B' = A$.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
$CaCO_3$	Na_2CO_3	1.0593	0.9441	$CaSO_4$	$CaCl_2$	0.8153	1.2265
$CaCO_3$	HCl	0.7288	1.3720	$CaSO_4$	CaF_2	0.5735	1.7438
CaF_2	AlF_3	0.7182	1.3925	$CaSO_4$	CaO	0.4119	2.4280
CaF_2	CaO	0.5128	1.9501	$CaSO_4$	F	0.2791	3.5827
CaF_2	$CaSO_4$	1.7438	0.5735	$CaSO_4$	HF	0.2539	3.4021
CaF_2	F	0.4867	2.0545	$CaSO_4$	H_2SO_4	0.7205	1.3875
CaF_2	HF	0.5126	1.9508	$CaSO_4$	SO_3	0.5881	1.7003
CaF_2	H_2SiF_6	1.8485	0.5410	$CaSO_4 \cdot 2H_2O$	CaO	0.3257	3.0707
CaF_2	NaF	1.0760	0.9294				
$Ca(HCO_3)_2$	CaO	0.3459	2.8908	Cb	Cb_2O_5	1.4278	0.7004
$Ca(HCO_3)_2$	CO_2	0.5429	1.8419				
$CaHPO_4$	CaO	0.4119	2.4276	Cd	CdO	1.1426	0.8754
$CaHPO_4$	$Ca_2P_2O_7$	0.9338	1.0709	Cd	CdS	1.2853	0.7780
$CaHPO_4$	P_2O_5	0.5219	1.9161	Cd	$CdSO_4$	1.8547	0.5392
$Ca(H_2PO_4)_2$	$NaHCO_3$	0.7175	1.3938	Cd	S	0.2853	3.5048
$Ca(H_2PO_4)_2$	P_2O_5	0.6067	1.6483	CdO	CdS	1.1251	0.8888
$CaH_2P_2O_7$	$Ca(H_2PO_4)_2$	1.0827	0.9236	CdS	H_2S	0.2327	4.2975
$CaH_2P_2O_7$	CaO	0.2594	3.8553	CdS	S	0.2220	4.5048
$CaH_2P_2O_7$*	$NaHCO_3$	0.7773	1.2866				
$CaH_2P_2O_7$	P_2O_5	0.6573	1.5214	Ce	$Ce(NO_3)_4$	2.7685	0.3612
$Ca(HSO_3)_2$	CaO	0.2773	3.6067	Ce	Ce_2O_3	1.1711	0.8539
$Ca(HSO_3)_2$	SO_2	0.6336	1.5783	Ce	CeO_2	1.2282	0.8142
$Ca(NO_3)_2$	N_2O_5	0.6582	1.5192	Ce	$Ce(SO_4)_2$	2.0275	0.4932
CaO	Ca	0.7146	1.3993	Ce_2O_3	CeO_2	1.0487	0.9536
CaO	$Ca(CH_3CO_2)_2$	2.8200	0.3546				
CaO	$CaCl_2$	1.9795	0.5052	CH_2ClCO_2H	Cl	0.3753	2.6645
CaO	$CaCO_3$	1.7847	0.5603	CH_3CHOH			
CaO	CaF_2	1.3924	0.7182	CO_2H	H_2SO_4	0.5446	1.8361
CaO	$Ca(HCO_3)_2$	2.8908	0.3459	CH_3CO_2H	$Ca(CH_3CO_2)_2$	1.3169	0.7594
CaO	$Ca(H_2PO_4)_2$	4.1766	0.2394	CH_3CO_2H	CH_3CO_2Na	1.3663	0.7319
CaO	$CaH_2P_2O_7$	3.8553	0.2594	CH_3CO_2H	$(CH_3CO)_2O$	0.8499	1.1766
CaO	$Ca(HSO_3)_2$	3.6067	0.2773	CH_3CO_2H	H_2SO_4	0.8169	1.2241
CaO	$Ca_3P_2O_8$	1.8446	0.5421	CH_3CO_2H	Na_2CO_3	0.8828	1.1327
CaO	$CaSO_3$	2.1427	0.4667	CH_3CO_2H	Na_2O	0.5164	1.9365
CaO	$CaSO_4$	2.4280	0.4119	CH_3CO_2H	Pb	1.7249	0.5797
CaO	$CaSO_4 \cdot 2H_2O$	3.0707	0.3257	CH_3CO_2Na	H_2SO_4	0.5979	1.6725
CaO	CH_3CO_2H	2.1413	0.4670	CH_3CO_2Na	Na_2O	0.3779	2.6459
CaO	CO_2	0.7874	1.2743	CH_3CO_2Na	Na_2SO_4	0.8660	1.1547
CaO	H_2SO_4	1.7494	0.5716	$(CH_3CO)_2O$	H_2SO_4	0.9612	1.0404
CaO	NaCl	2.0852	0.4796	$C_2H_2O_4$	H_2SO_4	1.0897	0.9177
CaO	Na_2CO_3	1.8905	0.5290	$C_2H_2O_4 \cdot 2H_2O$	H_2SO_4	0.7782	1.2851
CaO	Na_2SO_4	2.5338	0.3947	$C_4H_6O_6$	H_2SO_4	0.6537	1.5298
CaO	S	0.5720	1.7484	$C_4H_6O_6$	$NaHCO_3$	1.1197	0.8931
CaO	SO_3	1.4280	0.7003	$C_4H_4O_6HK$	H_2SO_4	0.2607	3.8362
$Ca_3P_2O_8$	CaO	0.5421	1.8446				
$Ca_3P_2O_8$	$Mg_2P_2O_7$	0.7178	1.3932	Cl	Ag	3.0423	0.3287
$Ca_3P_2O_8$	$(NH_4)_3PO_4 \cdot 12MoO_3$	12.102	0.0826	Cl	AgCl	4.0423	0.2474
				Cl	$AgNO_3$	1.7910	0.2088
$Ca_3P_2O_8$	P_2O_5	0.4579	2.1839	Cl	$AlCl_3$	1.2547	0.7970
CaS	$BaSO_4$	3.2347	0.3091	Cl	$BaCrO_4$	3.57 1	0.2798
$CaSO_3$	$BaSO_4$	1.9429	0.5147	Cl	CH_2ClCO_2H	2.6645	0.3753
$CaSO_3$	CaO	0.4667	2.1427	Cl	Ca	0.5653	1.7690
$CaSO_4$	$BaSO_4$	1.7147	0.5832	Cl	$CaCl_2$	1.5650	0.6390

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein indicator.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
Cl	CsCl	4.7454	0.2107	CO_2	$Mg(HCO_3)_2$	1.6629	0.6013
Cl	HCl	1.0284	0.9724	CO_2	MgO	0.9164	1.0913
Cl	H_2SO_4	1.3831	0.7230	CO_2	$MnCO_3$	2.6121	0.3828
Cl	I	3.5792	0.2794	CO_2	$Mn(HCO_3)_2$	2.0108	0.4973
Cl	K	1.1027	0.9069	CO_2	MnO	1.6121	0.6203
Cl	KCl	2.1027	0.4756	CO_2	Na_2CO_3	2.4091	0.4151
Cl	$KClO_3$	3.4563	0.5386	CO_2	$NaHCO_3$	1.9093	0.5238
Cl	$KClO_4$	3.9075	0.5919	CO_2	Na_2SO_4	3.6667	0.2727
Cl	Li	0.1974	5.0657	CO_2	Na_2O	1.4091	0.7097
Cl	Mg	0.3429	2.9162	CO_2	$(NH_4)_2CO_3$	2.1836	0.4579
Cl	$MgCl_2$	1.3429	0.7447	CO_2	$PbCO_3$	6.0705	0.1647
Cl	$MgCl_2 \cdot 6H_2O$	2.8672	0.3488	CO_2	Rb_2CO_3	5.2477	0.1906
Cl	MgO in $MgCl_2$	0.5685	1.7590	CO_2	$RbHCO_3$	3.3273	0.3006
				CO_2	Rb_2O	4.2478	0.2354
Cl	MnO_2	1.2257	0.8158	CO_2	$SrCO_3$	3.3551	0.2981
Cl	Na	0.6486	1.5417	CO_2	$Sr(HCO_3)_2$	2.3823	0.4198
Cl	NaCl	1.6486	0.6066	CO_2	SrO	2.3550	0.4246
Cl	$NaClO_3$	3.0023	0.3331	CO_2	$ZnCO_3$	2.8493	0.3510
Cl	$NaClO_4$	3.4535	0.2896				
Cl	NH_4	0.5088	1.9656	Cr	$BaCrO_4$	4.8651	0.2055
Cl	NH_4Cl	1.5088	0.6628	Cr	Cr_2O_3	1.4606	0.6846
Cl	Rb	2.4098	0.4150	Cr	$PbCrO_4$	6.2136	0.1609
Cl	RbCl	3.4098	0.2933	Cr	$K_2Cr_2O_7$	2.8029	0.3535
Cl	Sn in $SnCl_4$	0.8390	1.1919	Cr_2O	$BaCrO_4$	3.3308	0.3002
Cl	$SnCl_4$	1.8390	0.5438	Cr_2O	CrO_3	1.3157	0.7602
Cl	$PbCl_2$	3.9202	0.2551	Cr_2O	$PbCrO_4$	4.2513	0.2352
Cl	$PbCrO_4$	4.5572	0.2194	CrO_3	$BaCrO_4$	2.5322	0.3949
Cl	$ZnCl_2$	1.9217	0.5204	CrO_3	K_2CrO_4	1.9411	0.5152
				CrO_3	$K_2Cr_2O_7$	1.4706	0.6800
Co	$CoNO_3 \cdot 6H_2O$	4.9361	0.2026	CrO_3	$PbCrO_4$	3.2233	0.3097
Co	$Co(NO_2)_3(KNO_2)_3$	7.6706	0.1304				
				Cs	C Cl	1.2670	0.7893
Co	CoO	1.2714	0.7866	Cs	Cs_2O	1.0602	0.9432
Co	Co_3O_4	1.3053	0.7661	Cs	Cs_2CO_3	1.2258	0.8157
Co	$CoSO_4 \cdot 7H_2O$	4.7677	0.2097	Cs	Cs_2SO_4	1.3617	0.7344
CoO	Co_3O_4	2.0680	0.9336	$CsPtCl_6$	Cs	0.3945	2.5351
				$CsPtCl_6$	Cs_2O	0.4182	2.3911
CO_2	$BaCO_3$	4.4857	0.2229				
CO_2	BaO	3.4857	0.2869	Cu	CuO	1.2517	0.7989
CO_2	$Ba(HCO_3)_2$	2.9476	0.3393	Cu	Cu_2O	1.1258	0.8888
CO_2	C	0.2727	3.6667	Cu	Cu_2S	1.2522	0.7986
CO_2	$CaCO_3$	2.2743	0.4397	Cu	$CuSO_4$	2.5112	0.3982
CO_2	$Ca(HCO_3)_2$	1.8419	0.5429	Cu	$CuSO_4 \cdot 5H_2O$	3.9283	0.2546
CO_2	CaO	1.2743	0.7847	CuCNS	Cu	0.5226	1.9137
CO_2	CO_3	1.3636	0.7333	CuCNS	CuO	0.6541	1.5288
CO_2	$CsCO_3$	7.4005	0.1351	CuO	$CuSO_4$	2.0062	0.4985
CO_2	$FeCO_3$	2.6327	0.3798	CuO	H_2SO_4	1.2327	0.8112
CO_2	$Fe(HCO_3)_2$	2.0211	0.4948	CuO	$CuSO_4 \cdot 5H_2O$	3.1383	0.3186
CO_2	H_2SO_4	2.2292	0.4486	CuS	S	0.3353	2.9822
CO_2	K_2CO_3	3.1409	0.3184	Cu_2S	CuO	0.9996	1.0004
CO_2	K_2O	2.1409	0.4671	Cu_2S	Cu_2O	0.8991	1.1122
CO_2	$LiCO_3$	1.6818	0.5946				
CO_2	$LiHCO_3$	1.5457	0.6470	Er_2O_3	Er	0.8746	1.1433
CO_2	Li_2O	0.6818	1.4667				
CO_2	$MgCO_3$	1.9164	0.5218	F	$BaSiF_6$	2.4533	0.4076

$A \times A' = B$ and $B \times B' = A$.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
F	CaF_2	2.0545	0.4868	FeS_2	S	0.5346	1.8706
F	$CaSO_4$	3.5827	0.2791	$FeSO_4$	H_2SO_4	0.6457	1.5487
F	HF	1.0531	0.9496	$FeSO_4 \cdot 7H_2O$	H_2SO_4	0.3528	2.8345
F	H_2SiF_6	1.2660	0.7899	$Fe_2(SO_4)_3$	H_2SO_4	0.7358	1.3590
F	K_2SiF_6	1.9342	0.5170	$FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$	$Na_2Cr_2O_7$	0.1114	8.9808
F	NaF	2.2105	0.4524				
Fe	$FeCl_2$	2.2701	0.4405	Ga_2O_3	Ga	0.7444	1.3434
Fe	$FeCl_3 \cdot 6H_2O$	4.8410	0.2066	Ga_2S_3	Ga	0.5923	1.6882
Fe	$Fe(HCO_3)_2$	3.1851	0.3140				
Fe	FeO	1.2865	0.7773	GeO_2	Ge	0.6938	1.4414
Fe	Fe_2O_3	1.4298	0.6994	K_2GeF_6	Ge	0.2739	3.6510
Fe	Fe_3O_4	1.3820	0.7236				
Fe	$FePO_4$	2.7020	0.3701	GlO	Gl	0.3626	2.7582
Fe	FeS	1.5743	0.6352	GlO	$GlCl_2$	3.1881	0.3137
Fe	$FeSO_4$	2.7205	0.3676	GlO	$GlSO_4 \cdot 4H_2O$	7.0607	0.1416
Fe	$FeSO_4 \cdot 7H_2O$	4.9789	0.2008				
Fe	$Fe_2(SO_4)_3$	3.5807	0.2793	H	H_2O	8.9363	0.1119
Fe	$FeSO_4(NH_4)_2$ SO_4	7.0225	0.1424	H_3BO_3	B_2O_3	0.5643	1.7721
Fe (titr. equiv.)	HNO_3	0.5643	1.7721	HBr	Ag	1.3324	0.7505
Fe	$Na_2Cr_2O_7$	0.7820	1.2788	HBr	AgBr	2.3195	0.4311
$FeCO_3$	CO_2	0.3798	2.6327	HCl	AgCl	3.9305	0.2544
$Fe(HCO_3)_2$	CO_2	0.4948	2.0211	HCl	$CaCO_3$	1.3720	0.7288
FeO	Al_2O_3	0.4742	2.1088	HCl	Cl	0.9724	1.0284
FeO	$FeCO_3$	1.6125	0.6202	HCl	HNO_2	1.2893	0.7756
FeO	$Fe(HCO_3)_2$	2.4757	0.4039	HCl	HNO_3	1.7280	0.5787
FeO	Fe_2O_3	1.1114	0.8998	HCl	H_2SO_3	1.1255	0.8885
FeO	$FePO_4$	2.1002	0.4761	HCl	H_2SO_4	1.3448	0.7436
FeO	FeS	1.2237	0.8172	HCl	KCl	2.0445	0.4891
FeO	$FeSO_4$	2.1146	0.4729	HCl	K_2O	1.2915	0.7743
FeO	$FeSO_4 \cdot 7H_2O$	3.8700	0.2584	HCl	NaCl	1.6030	0.6239
FeO	H_2SO_4	1.3653	0.7324	HCl	Na_2CO_3	1.4533	0.6881
FeO	SO_3	1.1146	0.8972	HCl	NH_4Cl	1.4669	0.6817
Fe_2O_3	Al_2O_3	0.6400	1.5625	HCl	$SnCl_4$	1.7882	0.5592
Fe_2O_3	$FeCl_3$	2.0318	0.4922				
Fe_2O_3	$FeCO_3$	1.4509	0.6892	HCO_2H	H_2SO_4	1.0658	0.9383
Fe_2O_3	$Fe(HCO_3)_2$	2.2277	0.4489				
Fe_2O_3	Fe_3O_4	0.9666	1.0346	HF	$BaSiF_6$	2.3297	0.4292
Fe_2O_3	$FePO_4$	1.8898	0.5292	HF	CaF_2	1.9508	0.5126
Fe_2O_3	FeS	1.1011	0.9082	HF	$CaSO_4$	3.4021	0.2939
Fe_2O_3	FeS_2	1.5028	0.6655	HF	F	0.9496	1.0531
Fe_2O_3	$FeSO_4$	1.9027	0.5256	HF	H_2SO_4	2.4510	0.4080
Fe_2O_3	$FeSO_4 \cdot 7H_2O$	3.4822	0.2872	HF	K_2SiF_6	1.8368	0.5444
Fe_2O_3	$FeSO_4(NH_4)_2$ $SO_4 \cdot 6H_2O$	4.9118	0.2036	HF(2HF)	H_2SiF_6	3.6065	0.2773
				HF(6HF)	H_2SiF_6	1.2022	0.8318
Fe_2O_3	$Fe_2(SO_4)_3$	2.5032	0.3993				
Fe_2O_3	H_2SO_4	1.8428	0.5427	Hg	HgCl	1.1768	0.8498
Fe_2O_3	SO_3	1.5032	0.6648	Hg	$HgCl_2$	1.3535	0.7388
$FePO_4$	P_2O_5	0.4708	2.1229	Hg	HgO	1.0798	0.9261
FeS	$BaSO_4$	2.6554	0.3766	Hg	HgS	1.1599	0.8622
FeS	H_2S	0.3877	2.5791	HgCl	$SnCl_2$	0.4023	2.4859
FeS	H_2SO_4	1.1155	0.9863	HgCl	$SnCl_4$	0.5525	1.8100
FeS	S	0.3648	2.7431	$HgCl_2$	HgCl	0.8694	1.1502
FeS_2	Fe_2O_3	0.6654	1.5029	$HgCl_2$	HgS	0.8569	1.1670

$A \times A' = B$ and $B \times B' = A$.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
HgO	HgCl	1.1827	0.8455	H_2SiF_6	$BaSiF_6$	1.9379	0.5160
Hg_2O	HgCl	1.1321	0.8834	H_2SiF_6	CaF_2	0.54 0	1.8485
HgS	$Hg(CN)_2$	1.0860	0.9208	H_2SiF_6	F	0.7899	1.2660
HgS	$HgNO_3$	1.1290	0.8857	H_2SiF_6	2HF	0.2773	3.6065
HgS	$Hg(NO_3)_2$	1.3962	0.7162	H_2SiF_6	6HF	0.8318	1.2022
HgS	Hg_2O	0.8963	1.1158	H_2SiF_6	H_2SO_4	2.0391	0.4904
HgS	HgO	0.9307	1.0744	H_2SiF_6	K_2SiF_6	1.5279	0.6545
HgS	$HgSO_4$	1.2758	0.7838	H_2SiF_6	SiF_4	0.7227	1.3837
				H_2SiF_6	SiF_6	0.9860	1.0141
HI	Ag	0.8433	1.1859	H_2SiO_3	SiO_2	0.7699	1.2988
HI	AgI	1.8354	0.5448				
HI	Pd	0.4170	2.3979	H_2SO_3	$BaSO_4$	2.8437	0.3517
HI	PdI_2	1.4092	0.7097	H_2SO_3	HCl	0.8885	1.1255
HI	Tl	2.5868	0.3866	H_2SO_3	H_2SO_4	1.1949	0.8369
				H_2SO_3	SO_2	0.7805	1.2812
HNO_3	$AgNO_3$	3.2729	0.3055				
HNO_3	HCl	0.7756	1.2893	H_2SO_4	$AlCl_3$	0.9072	1.1023
HNO_3	H_2SO_4	1.0431	0.9587	H_2SO_4	Al_2O_3	0.3473	2.8792
HNO_3	NO	0.6382	1.5667	H_2SO_4	$Al_2(SO_4)_3$	1.1636	0.8594
HNO_3	Cl	.5627	1.7772	H_2SO_4	$Ba(OH)_2$	1.7473	0.5723
HNO_3	HCl	0.5787	1.7280	H_2SO_4	$BaSO_4$	2.3800	0.4202
HNO_3	H_2SO_4	0.7782	1.2850	H_2SO_4	C(in $BaCO_3$)	0.1223	8.1740
HNO_3	KNO_3	1.6045	0.6233	H_2SO_4	$Ca(CH_3CO_2)_2$	1.6120	0.6203
HNO_3	N	0.2223	4.4981	H_2SO_4	CaO	0.5716	1.7494
HNO_3	$NaNO_3$	1.3490	0.7413	H_2SO_4	$CaSO_4$	1.3878	0.7205
HNO_3	NH_3	0.2702	3.7006	H_2SO_4	CH_3CHOH		
HNO_3	NH_4Cl	0.8489	1.1780		CO_2H	1.8361	0.5446
HNO_3	$(NH_4)_2PtCl_6$	3.5215	0.2840	H_2SO_4	CH_3CO_2H	1.2241	0.8169
HNO_3	NO	0.4 62	2.0999	H_2SO_4	CH_3CO_2Na	1.6725	0.5979
HNO_3	N_2O_3	0.6032	1.6579	H_2SO_4	$(CH_3CO_2)_2O$	1.0404	0.9612
HNO_3	N_2O_4	0.7301	1.3697	H_2SO_4	$C_2H_2O_4$	0.9177	1.0897
HNO_3	N_2O_5	0.8571	1.1668	H_2SO_4	$C_2H_2O_4 \cdot 2H_2O$	1.2851	0.7782
HNO_3	Pt	1.5471	0.6464	H_2SO_4	$C_4H_6O_6$	1.5298	0.6537
				H_2SO_4	Cl_2	0.7230	1.3831
H_3PO_4	HPO_3	0.8163	1.2251	H_2SO_4	CO_2	0.4487	2.2287
H_3PO_4	$H_4P_2O_7$	0.9081	1.1012	H_2SO_4	$CuSO_4$	1.6275	0.6144
H_3PO_4	H_2SO_4	1.0002	0.9998	H_2SO_4	Fe	0.5203	1.9220
H_3PO_4	$Mg_2P_2O_7$	1.1356	0.8806	H_2SO_4	FeO	0.7324	1.3653
H_3PO_4	P	0.3165	3.1593	H_2SO_4	Fe_2O_3	0.5427	1.8428
H_3PO_4	P_2O_5	0.7244	1.3804	H_2SO_4	FeS	0.8963	1.1155
H_2PtCl_6				H_2SO_4	$FeSO_4$	1.5487	0.6457
$\cdot 6H_2O$	Pt	0.376	2.6558	H_2SO_4	$FeSO_4 \cdot 7H_2O$	2.8345	0.3528
				H_2SO_4	$Fe_2(SO_4)_3$	1.3590	0.7358
H_2S	As_2S_3	2.4074	0.4154	H_2SO_4	H_3AsO_4	0.9648	1.0365
H_2S	$BaSO_4$	6.8493	0.1460	H_2SO_4	HCl	0.7436	1.3448
H_2S	CdS	4.2379	0.2360	H_2SO_4	$H_2C_2O_4$	0.9177	1.0898
H_2S	FeS	2.5791	0.3877	H_2SO_4	HCO_2H	0.9383	1.0658
H_2S*	H_2SO_4	1.4388	0.6950	H_2SO_4	HF	0.4080	2.4510
H_2S	S	).9388	1.0629	H_2SO_4	HNO_2	0.9587	1.0431
H_2S	SO_2	1.8835	0.5309	H_2SO_4	HNO_3	1.2850	0.7782
H_2S	SO_3	2.3488	0.4258	H_2SO_4*	H_3PO_4	0.9998	1.0002
				H_2SO_4*	H_2S	0.6950	1.4388
H_2SeO_3	Se	0.6129	1.6315	H_2SO_4*	H_2SO_3	0.8369	1.1949

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
H_2SO_4	H_2SiF_6	0.4904	2.0391	I	KI	1.3081	0.7645
H_2SO_4	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	3.2253	0.3101	I	KIO_3	1.6863	0 5930
				I	$NaIO_3$	1.55 4	0 6413
H_2SO_4	$KHC_4H_4O_6$	3.8362	0.2607	I	Na_2SO_3	0.4967	2 0135
H_2SO_4	KNO_3	2.0617	0.4850	I	Pd	0.4203	2.3790
H_2SO_4	K_2O	0.9604	1.0413	I	PdI_2	1.4204	0.7040
H_2SO_4	KOH	1.1442	0.8740	I	Tl	2.6074	0.3835
H_2SO_4	K_2SiF_6	0.7493	1.3345				
H_2SO_4	K_2SO_4	1.7767	0.5628	In	In_2O_3	1.2090	0 8271
H_2SO_4	MgO	0.4111	2.4325	In	In_2S_3	1.4187	0.7047
H_2SO_4	$MgSO_4$	1.2274	0.8147				
H_2SO_4	NaCl	1.1920	0.8389	Ir	Ir_2O_3	1.2491	0.8006
H_2SO_4†	Na_2CO_3	1.0808	0.9252				
H_2SO_4	$Na_2C_2O_4$	1.3661	0.7320	K	K_2O	1.2046	0.8302
H_2SO_4	$Na_2Cr_2O_7$	2.6711	0.3744	K	K_2PtCl_6	6.2143	0.1609
H_2SO_4†	$NaHCO_3$	1.7132	0.5837	K	K_2SO_4	2.2285	0.4487
H_2SO_4*	NaH_2PO_4	2.4583	0.4068	$K_2Al_2(SO_4)_3 \cdot 24H_2O$	Al	0.0571	17.510
H_2SO_4†	Na_2HPO_4	2.8964	0.3453				
H_2SO_4	$NaHSO_3$	2.1222	0.4712	ditto	Al_2O_3	0.1077	9.2863
H_2SO_4	$NaNO_3$	1.7334	0.5769	ditto	H_2O	0.4561	2.1949
H_2SO_4	Na_2O	0.6321	1.5820	ditto*	H_2SO_4	0.3101	3.2253
H_2SO_4	NaOH	0.8158	1.2258	ditto (tot. I	H_2SO_4 (+Al +K)	0.4134	2.4190
H_2SO_4	Na_3PO_4	3.3448	0.2990				
H_2SO_4	Na_2S	0.7959	1.2564	ditto	S	0.1352	7.3984
H_2SO_4	Na_2SiF_6	0.9598	1.0418	ditto	K	0.0824	2.1363
H_2SO_4	Na_2SO_3	2.5706	0.3 90	$K_2Al_2(SO_4)_3$	$NaHCO_3$	0.9756	1.0251
H_2SO_4	Na_2SO_4	1.4404	0.6904	KBF_4	$Na_2B_4O_7 \cdot 10H_2O$	0.7570	1.3199
H_2SO_4	NH_3	0.3473	2.8792				
H_2SO_4	NH_4Cl	1.0909	0.9167	KBr	Br	0.6715	1.4892
H_2SO_4	$(NH_4)_2O$	0.5310	1.8382	KBr	K	0.3285	3.0440
H_2SO_4	$(NH_4)_2S$	0.6948	1.4392	KCl	Ag	1.4469	0.6911
H_2SO_4	$(NH_4)_2SO_4$	1.3473	0.7422	KCl	AgCl	1.9225	0.5202
H_2SO_4	$(NH_4)_2S_2O_8$	2.3268	0.4298	KCl	Cl	0.4756	2.1027
H_2SO_4	N_2O_3	0.7750	1.2903	KCl	HCl	0.4891	2.0445
H_2SO_4	N_2O_4	0.9382	1.0659	KCl	$KHC_4H_4O_6$	2.5233	0.3963
H_2SO_4	N_2O_5	1.1013	0.9080	KCl	K_2PtCl_4	3.2589	0.3069
H_2SO_4‡ (Y ppt.)	P	0.0275	36.364	KCl	K_2SO_4	1.1686	0.8557
				KCl	Pt	2.4935	0.4010
H_2SO_4	P_2O_5	0.7243	1.3806	KCl	$KClO_3$	1.1696	0.8550
H_2SO_4‡ (Y ppt.)	P_2O_5	0.0629	15.878	KCN	AgCN	2.0564	0.4863
				KCN	AgCl	1.1696	0.8550
H_2SO_4	S	0.3267	3.0590	K_2CO_3	CO_2	0.3184	3.1409
H_2SO_4†	SO_2	0.6532	1.5309	K_2CO_3	KOH	0.8120	1.2315
H_2SO_4*	SO_2	1.3064	0.7655	K_2CO_3	K_2SO_4	1 2610	0.7930
H_2SO_4	SO_3	0.8163	1.2250	K_2CrO_4	$BaCrO_4$	1.3046	0.7666
H_2SO_4	$S_2O_5Cl_2$	0.7309	1.3683	K_2CrO_4	CrO_3	0.5153	1.9411
H_2SO_4	SO_3HCl	0.7921	1.2625	$K_2Cr_2O_7$	$BaCrO_4$	1.7220	0.5807
H_2SO_4	Zn	0.6665	1.5004	$K_2Cr_2O_7$	CrO_3	0.6800	1.4706
H_2SO_4	ZnO	0.8296	1.2054	$K_2Cr_2O_7$	Fe	1.1388	0.8782
H_2SO_4	$ZnSO_4$	1.6459	0.6076	$K_2Cr_2O_7$	K_2O	0.3200	3.1252
				$KHCO_3$	CO_2	0.4395	2.2752
I	AgI	1.8500	0.5405	$KHSO_4$	$BaSO_4$	1.7141	0.5834
I	Cl	0.2794	3.5792	KI	I	0.7645	3.0440

A×A′=B and B×B′=A.

* Phenolphthalein. † Methyl Orange.

‡ Titration of yellow precipitate, ammonium phosphomolybdate.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
KI	K	0.2355	4.2460	La	La_2O_3	1.1727	0.8528
$KMnO_4$	Mn_2O_4	0.4826	2.0721				
KNO_3	H_2SO_4	0.4850	2.0617	Li	LiCl	6.1096	0.1637
KNO_3	K_2PtCl_6	2.4041	0.4159	Li	Li_2CO_3	5.3227	0.1879
KNO_3	$NaNO_3$	0.8408	1.1894	Li	Li_2O	2.1539	0.4643
KNO_3	NO	0.2968	3.6898	Li	Li_3PO_4	5.5629	0.1798
KNO_3	N_2O_5	0.5342	1.8721	LiCl	Li_2SO_4	7.1296	0.1262
KOH	H_2SO_4	0.8741	1.1440	LiCl	Li_2O	0.3523	2.8381
KOH	K_2CO_3	1.2315	0.8120	Li_2O	Li_2CO_3	2.4630	0.4044
KOH	K_2O	0.8394	1.1913	Li_2O	Li_2SO_4	3.6799	0.2718
K_2O	Cl	0.7529	1.3282	Li_2O	Li_3PO_4	2.5842	0.3870
K_2O	CO_2	0.4671	2.1409	Li_3PO_4	Li_2CO_3	0.9569	1.0451
K_2O	HCl	0.7743	1.2915	Li_3PO_4	$LiHCO_3$	1.7601	0.5682
K_2O	H_2SO_4	1.0413	0.9604	Li_3PO_4	Li_2SO_4	1.4240	0.7023
K_2O	K	2.8302	1.2046	Li_2SO_4	Li	0.1262	7.9216
K_2O	KBr	2.5270	0.3957	Li_2SO_4	LiCl	0.7712	1.2966
K_2O	KCl	1.5830	0.6317	Li_2SO_4	SO_3	0.7282	1.3732
K_2O	$KHCO_3$	1.0627	0.9410				
K_2O	K_2CO_3	1.4671	0.6816	Mg	Cl	2.9162	0.3429
K_2O	$KHC_4H_4O_6$	3.9936	0.2504	Mg	MgO	1.6579	0.6032
K_2O	$K_2Cr_2O_7$	3.1252	0.3200	Mg	$Mg_2P_2O_7$	4.5789	0.2184
K_2O	KI	3.5248	0.2837	Mg	$MgSO_4$	4.9450	0.2020
K_2O	KOH	1.1913	0.8394	$MgCl_2$	Cl	0.7447	1.3429
K_2O	KNO_3	2.1466	0.4658	$MgCl_2 \cdot 6H_2O$	Cl	0.3488	2.8672
K_2O	K_2PtCl_6	5.1609	0.1938	$MgCO_3$	CO_2	0.5218	1.9164
K_2O	K_2SO_4	1.8500	0.5406	$Mg(HCO_3)_2$	CO_2	0.6013	1.6629
K_2O	SO_3	0.8500	1.1765	MgO	$BaSO_4$	5.7897	0.1727
K_2PtCl_6	K	0.1609	6.2143	MgO	Cl	1.7590	0.5685
K_2PtCl_6	KCl	0.3068	3.2589	MgO	CO_2	1.0913	0.9164
K_2PtCl_6	K_2CO_3	0.2844	3.5162	MgO	H_2SO_4	2.4325	0.4111
K_2PtCl_6	KNO_3	0.4159	2.4041	MgO	$MgCl_2$	2.3621	0.4234
K_2PtCl_6	K_2O	0.1938	5.1609	MgO	$MgCO_3$	2.0913	0.4782
K_2PtCl_6	K_2SO_4	0.3585	2.7897	MgO	$Mg(HCO_3)_2$	3.6294	0.2755
K_2PtCl_6	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	1.9530	0.5120	MgO	$Mg_2P_2O_7$	2.7619	0.3621
				MgO	$MgSO_4$	2.9859	0.3349
K_2PtCl_6	$K_2Cr_2(SO_4)_4 \cdot 24H_2O$	2.0559	0.4964	MgO	Na_2SO_4	3.5236	0.2838
				MgO	S	0.7954	1.2572
K_2PtCl_6	Pt	0.4013	2.4921	MgO	SO_3	1.9859	0.5036
K_2PtCl_6	$PtCl_4$	0 6931	1.4427	$Mg_2P_2O_7$	$Ca_3(PO_4)_2$	1.3932	0.7178
K_2PtCl_6	$PtCl_4 \cdot 5H_2O$	0.8785	1.1383	$Mg_2P_2O_7$	H_3PO_4	0.8806	1.1356
K_2SiF_6	F	0.5170	1.9342	$Mg_2P_2O_7$	Mg	0.2184	4.5789
K_2SiF_6	HF	0.5444	1.8368	$Mg_2P_2O_7$	$Mg(CH_3CO_2)$	1.2784	0.7822
K_2SiF_6	H_2SiF_6	0.6545	1.5276	$Mg_2P_2O_7$	$MgCl_2$	0.8552	1.1692
K_2SiF_6	H_2SO_4	1.3345	0.7493	$Mg_2P_2O_7$	$MgCl_2 \cdot 6H_2O$	1.8260	0.5477
K_2SiF_6	KF	0.5270	1.8976	$Mg_2P_2O_7$	$MgCO_3$	0.7575	1.3203
K_2SiF_6	SiF_4	0.4730	2.1141	$Mg_2P_2O_7$	$Mg(HCO_3)_2$	1.3141	0.7610
K_2SiF_6	SiO_2	0.2735	3.6567	$Mg_2P_2O_7$	MgO	0.3621	2.7619
K_2SiO_3	SiO_2	0.3903	2.5622	$Mg_2P_2O_7$	$MgSO_4$	1.0811	0.9250
K_2SO_4	H_2SO_4	0.5628	1.7767	$Mg_2P_2O_7$	$MgSO_4 \cdot 7H_2O$	2.2143	0.4516
K_2SO_4	K	0.4487	2.2285	$Mg_2P_2O_7$	Na_3PO_4	1.4731	0.6789
K_2SO_4	KCl	0.8557	1.1686	$Mg_2P_2O_7$	Na_2HPO_4	1.2755	0.7840
K_2SO_4	K_2CO_3	0.7930	1.2610	$Mg_2P_2O_7$	Na_2SO_4	1.2758	0.7838
K_2SO_4	K_2O	0.5405	1.8500	$Mg_2P_2O_7$	$(NH_4)H_2PO_4$	1.0336	0.9675
K_2SO_4	K_2PtCl_6	2.7897	0.3585	$Mg_2P_2O_7$	$(NH_4)_2HPO_4$	1.1865	0.8428
K_2SO_4	SO_3	0.4595	2.1765	$Mg_2P_2O_7$	P	0.2787	3.5877

$A \times A' = B$ and $B \times B' = A$.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
$Mg_2P_2O_7$	P_2O_5	0.6379	1.5676	Na	NaI	6.5183	0.1534
$MgSO_4$	$BaSO_4$	1.9389	0.5158	Na	Na_2O	1.3478	0.7419
$MgSO_4$	H_2SO_4	0.8147	1.2274	Na	NaOH	1.7391	0.5750
$MgSO_4$	SO_3	0.6651	1.5036	Na	Na_2SO_3	2.6754	0.3738
$MgSO_4 \cdot 7H_2O$	SO_3	0.3248	3.0786	Na	Na_2SO_4	3.0885	0.3238
$MgSO_4 \cdot 7H_2O$	$BaSO_4$	0.9469	1.056	$Na_2Al_2O_4$	Al_2O_3	0.6224	1.6067
Mn	$MnCO_3$	2.0923	0.4779	$Na_2Al_2(SO_4)_4 \cdot 24H_2O$	S	0.1399	7.1474
Mn	MnO	1.2913	0.7744	$Na_2B_4O_7$	B_2O_3	0.6931	1.4429
Mn	Mn_2O_3	1.4369	0.6959	$Na_2B_4O_7$	H_3BO_3	1.2282	0.8142
Mn	Mn_3O_4	1.3884	0.7203	$Na_2B_4O_7 \cdot 10H_2O$	B_2O_3	0.1832	5.4594
Mn	$Mn_2P_2O_7$	2.5846	0.3869	ditto	H_3BO_3	0.6492	1.5404
Mn	MnS	1.5838	0.6314	ditto	KBF	1.3199	0.7577
$MnCO_3$	CO_2	0.3828	2.6121	NaBr	Ag	1.0458	0.9562
$Mn(HCO_3)_2$	CO_2	0.4973	2.0108	NaBr	AgBr	1.8247	0.5480
MnO	$MnCO_3$	1.6203	0.6172	NaBr	Br	0.7765	1.2878
MnO	Mn_2O_3	1.1128	0.8987	NaCl	A Cl	2.4519	0.4078
MnO	MnS	1.2266	0.8153	NaCl	$AgNO_3$	2.9061	0.3441
MnO	SO_3	1.1289	0.8859	NaCl	CaO	.4786	2.0852
Mn_2O_3	$KMnO_4$	2.0721	0.4826	NaCl	Cl	0.6066	1.6486
Mn_2O_3	Mn_3O_4	0.9662	1.0349	NaCl	HCl	0.6239	1.6030
Mn_2O_3	$MnSO_4$	2.0398	0.4902	NaCl	H_2SO_4	0.8389	1.1920
Mn_2O_3	S	0.2032	4.9224	NaCl	Na_2CO_3	0.9066	1.1030
Mn_3O_4	K_2MnO_4	2.5848	0.3869	NaCl	$NaHCO_3$	1.4370	0.6959
$MnSO_4$	$BaSO_4$	1.5458	0.6469	NaCl	Na_2HPO_4	1.2149	0.8231
$MnSO_4$	SO_3	0.5303	1.8858	NaCl	$NaHSO_3$	1.7803	0.5617
Mo	MoO_3	1.5000	0.6667	NaCl	Na_2O	0.5303	1.8858
Mo	MoS_2	2.0022	0.4995	NaCl	Na_2SO_4	1.2151	0.8230
Mo	$PbMoO_4$	3.8239	0.2615	NaCl	$ZnCl_2$	1.1656	0.8579
MoO_3	MoS_2	1.3348	0.7492	$NaClO_3$	Cl	0.3331	3.0023
MoO_3	$(NH_4)_2MoO_4$	1.3617	0.7344	$NaClO_4$	Cl	0.2896	3.4535
MoO_3	$(NH_4)_3PO_4(MoO_3)_{12}$	1.0863	0.9205	Na_2CO_3	$BaSO_4$	2.2022	0.4541
MoO_3	$PbMoO_4$	2.5494	0.3923	Na_2CO_3	$CaCO_3$	0.9441	1.0593
$MoO_4 \cdot (NH_4)_2$	$PbMoO_4$	1.8722	0.5342	Na_2CO_3	CaO	0.5290	1.8905
N	HNO_3	4.4981	0.2223	Na_2CO_3	CH_3CO_2H	1.1327	0.8828
N	NO_2	3.2841	0.3045	Na_2CO_3	CO_2	0.4151	2.4091
N	N_2O_3	2.7131	0.3686	Na_2CO_3	HCl	0.6881	1.4533
N	N_2O_4	3.2841	0.3045	Na_2CO_3	H_2SO_4	0.9253	1.0807
N	N_2O_5	3.8551	0.2594	Na_2CO_3	Na	0.4340	2.3044
N	$NaNO_3$	6.0678	0.1648	Na_2CO_3	NaCl	1.1030	0.9066
N	NH_3	1.2155	0.8227	Na_2CO_3	$NaHCO_3$	1.1850	0.6309
N	Pt	6.9665	0.1435	Na_2CO_3	$NaHSO_3$	1.9637	0.5092
N	SO_3	2.8576	0.3499	Na_2CO_3	NaOH	0.7549	1.3247
Na	Br	3.4748	0.2878	Na_2CO_3	Na_2O	0.5849	1.7097
Na	Cl	1.5417	0.6486	$Na_2C_2O_4$	H_2SO_4	0.7320	1.3661
Na	I	5.5182	0.1812	Na_2CrO_4	$PbCrO_4$	1.9944	0.5014
Na	NaBr	4.4747	0.2235	$Na_2Cr_2O_7$	Fe	1.2788	0.7820
Na	NaCl	2.5417	0.3934	$Na_2Cr_2O_7$	H_2SO_4	0.3744	2.6711
Na	Na_2CO_3	2.3044	0.4340	$Na_2Cr_2O_7$	Na_2CrO_4	1.2367	0.8086
Na	NaF	1.8261	0.5476	NaF	CaF_2	0.9294	1.0760
Na	$NaHCO_3$	3.6525	0.2740	Na_3HAsO_3	$Mg_3As_2O_7$	0.9135	1.0947
				Na_2HAsO_4	As	0.4031	2.4809
				Na_2HAsO_4	As_2O_5	0.6182	1.6177
				Na_2HAsO_4	$Mg_3As_2O_7$	0.8349	1.1978

$A \times A' = B$ and $B \times B' = A$.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
a_2HAsO_4...	As_2O_5.....	0.7011	1.4264	$NaNO_3$.....	NH_3.....	0.2004	4.9906
$aHCO_3$....	$Al_2(SO_4)_3$....	0.6793	1.4721	$NaNO_3$.....	NO.....	0.3530	2.8327
$aHCO_3$*...	$Ca(H_2PO_4)_2$..	1.3938	0.7175	$NaNO_3$.....	N_2O_5.....	0.6353	1.5740
$aHCO_3$*...	$CaH_2P_2O_7$...	1.2866	0.7773	NaOH.....	H_2SO_4.....	1.2258	0.8158
$aHCO_3$....	$C_4H_6O_6$.....	0.8931	1.1197	NaOH.....	Na_2O.....	0.7748	1.2906
$aHCO_3$....	CO_2.....	0.5238	1.9039	NaOH.....	Na_2SiF_6.....	0.8499	1.1766
$aHCO_3$....	H_2SO_4.....	0.5838	1.7129	NaOH.....	$(NH_4)_3PO_4$ $(MoO_3)_{12}$	2.0400	0.4902
$aHCO_3$....	$KHC_4H_4O_6$..	2.2395	0.4465	Na_2O.....	$BaSO_4$.....	3.7651	0.2656
$aHCO_3$....	$KMnO_4$.....	0.4717	2.1260	Na_2O.....	CH_3CO_2H...	1.9365	0.5164
$aHCO_3$....	Na.....	0.2740	3.6525	Na_2O.....	CH_3CO_2Na..	2.6459	0.3779
$aHCO_3$....	Na_2CO_3.....	1.2618	0.7925	Na_2O.....	H_2SO_4.....	1.582	0.6321
$aHCO_3$*...	NaH_2PO_4....	1.4291	0.6997	Na_2O.....	Na.....	0.7419	1.3478
$aHCO_3$*...	$Na_2H_2P_2O_4$...	1.3219	0.7565	Na_2O.....	NaCl.....	1.8858	0.5303
$aHCO_3$....	Na_2O.....	0.3690	2.7099	Na_2O.....	Na_2CO_3.....	1.7097	0.5849
aH_2PO_4*...	H_2SO_4.....	0.4068	2.4583	Na_2O.....	NaF.....	1.3548	0.7381
aH_2PO_4*...	$NaHCO_3$....	0.6997	1.4291	Na_2O.....	$NaHCO_3$....	2.7099	0.3690
aH_2PO_4*...	NaH_2PO_4 $\cdot 4H_2O$	1.6003	0.6249	Na_2O.....	Na_2HPO_4....	2.2911	0.4365
				Na_2O.....	NaH_2PO_4....	3.8728	0.2582
aH_2PO_4*...	Na_2O.....	0.2582	3.8728	Na_2O.....	$Na_2H_2P_2O_7$...	3.5822	0. 792
aH_2PO_4*...	P.....	0.2585	3.8678	Na_2O.....	$NaHSO_3$.....	3.3574	0.2979
aH_2PO_4*...	P_2O_5.....	0.5917	1.6900	Na_2O.....	$NaNO_3$.....	2.7423	0.3647
a_2HPO_4†...	H_2SO_4.....	0.3453	2.8964	Na_2O.....	NaOH.....	1.2906	0.7748
a_2HPO_4....	Na_2HPO_4 $\cdot 12H_2O$	2.5220	0.3965	Na_2O.....	Na_3PO_4.....	1.7639	0.5669
				Na_2O.....	Na_2S.....	1.2592	0.7942
a_2HPO_4....	Na_2O.....	0.4365	2.2911	Na_2O.....	Na_2SO_3.....	2.0334	0.4918
a_2HPO_4....	P_2O_5.....	0.5001	1.9995	Na_2O.....	Na_2SO_4.....	2.2915	0.4364
$a_2H_2P_2O_7$...	$NaHCO_3$....	0.7565	1.3219	Na_2O*.....	P_2O_5.....	1.1458	0.8727
$a_2H_2P_2O_7$...	Na_2O.....	0.2792	3.5822	Na_2O.....	SO_3.....	1.2915	0.7743
$a_2H_2P_2O_7$...	P_2O_5.....	0.6397	1.5632	Na_2S.....	$BaSO_4$.....	2.9904	0.3344
$a(NH_4)$ $HPO_4\cdot 4H_2O$	P_2O_5.....	0.3395	2.9452	Na_2S.....	H_2S.....	0.4237	2.3602
				Na_2S.....	H_2SO_4.....	1.2564	0.7959
a_3PO_4.....	H_2SO_4.....	0.2990	3.3448	Na_2S.....	Na_2O.....	0.7942	1.2592
a_3PO_4.....	$Mg_2P_2O_7$.....	0.6789	1.4731	Na_2S.....	S.....	0.4108	2.4343
a_3PO_4.....	Na_2O.....	0.5669	1.7639	Na_2SO_3.....	$BaSO_4$.....	1.8515	0.5401
a_3PO_4.....	Na_2SO_4.....	1.2991	0.7698	Na_2SO_3.....	H_2SO_4.....	0.3890	2.5706
a_3PO_4....	Na_3PO_4 $\cdot 12H_2O$	2.3179	0.4314	Na_2SO_3.....	I.....	2.0135	0.4966
				Na_2SO_3.....	Na_2O.....	0.4918	2.0334
a_3PO_4.....	P_2O_5.....	0.4331	2.3091	Na_2SO_3.....	SO_2.....	0.5082	1.9677
$aHSO_3$.....	$BaSO_4$.....	2.2432	0.4485	$Na_2SO_4\cdot 7H_2O$	SO_2.....	0.2541	3.9360
$aHSO_3$.....	H_2SO_4.....	0.4712	2.1222	$Na_2S_2O_3$.....	$BaSO_4$.....	2.9524	0.3387
$aHSO_3$.....	NaCl.....	0.5617	1.7803	$Na_2S_2O_3$.....	$Na_2S_2O_3$ $\cdot 5H_2O$	1.5696	0.6371
$aHSO_3$.....	Na_2O.....	0.2979	3.: 574				
$aHSO_3$.....	$Na_2S_2O_5$.....	0.9134	1.0948	Na_2SO_4.....	$BaSO_4$.....	1.6431	0.6086
$aHSO_3$.....	SO_3.....	6.6156	1.6244	Na_2SO_4.....	CaO.....	0.3947	2.5338
NaI.....	Na.....	0.1534	6.5183	Na_2SO_4.....	CH_3CO_2Na..	1.1547	0.8660
NaI.....	Na_2O.....	0.2068	4.8350	Na_2SO_4.....	H_2SO_4.....	0.6904	1.4484
aIO_3.....	I.....	0.6413	1.5594	Na_2SO_4.....	MgO.....	0.2838	3.5236
aNO_3.....	HNO_3.....	0.7413	1.3490	Na_2SO_4.....	$Mg_2P_2O_7$.....	0.7838	1.2758
aNO_3.....	H_2SO_4.....	0.5769	1.7334	Na_2SO_4.....	Na.....	0.3238	3.0835
aNO_3.....	KNO_3.....	1.1894	0.8408	Na_2SO_4.....	NaCl.....	0.8230	1.2151
aNO_3.....	$NaNO_2$.....	0.8117	1.2319	Na_2SO_4.....	Na_2CO_3.....	0.7461	1.3403
aNO_3.....	Na_2O.....	0.3647	2.7423	Na_2SO_4.....	NaF.....	0.5913	1.6905

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein. † Methyl Orange.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
Na_2SO_4	$NaHSO_3$	1.4652	0.6825	Ni	$NiSO_4 \cdot 7H_2O$	4.7863	0.2089
Na_2SO_4	Na_2O	0.4364	2.2915				
Na_2SO_4	Na_2S	0.5495	1.8198	NO	HNO_2	1.5667	0.6382
Na_2SO_4	Na_2SO_3	0.8874	1.1269	NO	HNO_3	2.0999	0.4762
Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$	2.2681	0.4409	NO	KNO_3	3.3689	0.2968
				NO	$NaNO_3$	2.8327	0.3530
Na_2SO_4	SO_3	0.5636	1.7743	1cc NO = 0.0021 g. HNO_2, or 0.0028143 g. HNO_3, or 0.00415 g. KNO_3, or 0.003796 g. $NaNO_3$, or 0.00134 g. NO, or 0.001696 g. N_2O_3, or 0.0020545 g. N_2O_4.			
Nd	Nd_2O_3	1.1674	0.8566				
NH_3	HNO_3	3.6995	0.2704				
NH_3	H_2SO_4	2.8792	0.3473				
NH_3	N	0.8227	1.2155	N_2O_3	$AgNO_3$	4.0487	0.2470
NH_3	$NaNO_2$	4.0513	0.2468	N_2O_3	HCl	0.9594	1.0423
NH_3	$NaNO_3$	4.9906	0.2005	N_2O_3	HNO_3	1.6579	0.6032
NH_3	NH_4Cl	3.1409	0.3184	N_2O_3*	H_2SO_3	1.0798	0.9261
NH_3	$(NH_4)_2HPO_4$	3.8785	0.2578	N_2O_3	H_2SO_4	1.2903	0.7750
NH_3	$(NH_4)H_2PO_4$	6.7570	0.1480	N_2O_3	N	0.3686	2.7131
NH_3	NH_4OH	2.0577	0.4860	N_2O_3	$NaNO_2$	2.0787	0.4810
NH_3	$(NH_4)_2PtCl_6$	13.032	0.0764	N_2O_3	NO	0.7895	1.2666
NH_3	$(NH_4)_2SO_4$	3.8790	0.2578	N_2O_3	N_2O_4	1.2104	0.8262
NH_3	N_2O_5	3.1714	0.3153	N_2O_3	HCl	0.7928	1.2617
$(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$	$_2Al_2O_3$	0.1127	8.8742	N_2O_4	HNO_3	1.3697	0.7301
ditto	S	0.1414	7.0696	N_2O_4*	H_2SO_3	0.9820	1.1210
NH_4Cl	AgCl	2.6793	0.3732	N_2O_4	H_2SO_4	1.0659	0.9382
NH_4Cl	Cl	0.6628	1.5088	N_2O_4	N	0.3045	3.2841
NH_4Cl	HCl	0.6817	1.4669	N_2O_4	NO	0.6523	1.5332
NH_4Cl	H_2SO_4	0.9167	1.0909	N_2O_5	HCl	0.6752	1.4810
$(NH_4)H_2PO_4$	$Mg_2P_2O_7$	0.9675	1.0336	N_2O_5	HNO_3	1.1668	0.8571
$(NH_4)H_2PO_4$	NH_3	0.1480	6.7570	N_2O_5*	H_2SO_3	0.7599	1.3159
$(NH_4)_2HPO_4$	$Mg_2P_2O_7$	0.8428	1.1865	N_2O_5	H_2SO_4	0.9080	1.1013
$(NH_4)_2HPO_4$	NH_3	0.2578	3.8785	N_2O_5	KNO_3	1.8721	0.5342
$(NH_4)_2O$	H_2SO_4	1.8832	0.5310	N_2O_5	$NaNO_3$	1.5740	0.6353
$(NH_4)_3PO_4(MoO_3)_{12}$	P	0.0165	C0.475	N_2O_5	NH_3	0.3153	3.1714
				N_2O_5	NO	0.5556	1.7997
ditto	P_2O_5	0.0378	26.424	Os	OsO_4	1.3353	0.7489
$(NH_4)_2PtCl_6$	HNO_3	0.2840	3.5215				
$(NH_4)_2PtCl_6$	Pt	0.4393	2.2761	P	H_3PO_4	3.1593	0.3165
$(NH_4)_2PtCl_6$	$PtCl_6$	0.7589	1.3177	P	$Mg_2P_2O_7$	3.5877	0.2787
$(NH_4)_2S$	H_2SO_4	1.4392	0.6948	P	NaH_2PO_4	3.8678	0.2585
$(NH_4)_2SO_4$	$BaSO_4$	1.7665	0.5661	P	$(NH_4)_3PO_4(MoO_3)_{12}$	C0.476	0.0165
$(NH_4)_2SO_4$	H_2SO_4	0.7422	1.3473				
$(NH_4)_2SO_4$	N	0.2120	4.7162	P	P_2O_5	2.2887	0.4369
$(NH_4)_2SO_4$	NH_3	0.2578	3.8790	P_2O_5	$AlPO_4$	1.7197	0.5815
$(NH_4)_2SO_4$	N_2O_3	0.8174	1.2234	P_2O_5	$Al_2P_2O_8$	1.7193	0.5816
$(NH_4)_2S_2O_8$	H_2SO_4	0.4298	2.3268	P_2O_5	$CaHPO_4$	1.9161	0.5219
				P_2O_5	$Ca(H_2PO_4)_2$	1.6483	0.6067
Ni	$NiC_8H_{14}N_4O_4$	4.9221	0.2032	P_2O_5	$CaH_2P_2O_7$	1.5214	0.6573
Ni	$Ni(NO_3)_2 \cdot 6H_2O$	4.9556	0.2018	P_2O_5	$Ca_2P_2O_8$	2.1839	0.4579
				P_2O_5	$FePO_4$	2.1239	0.4708
Ni	NiO	1.2727	0.7858	P_2O_5	H_3PO_4	1.3804	0.7244
Ni	$NiSO_4$	2.6371	0.3792	P_2O_5	H_2SO_4	1.3806	0.7243

A × A′ = B and B × B′ = A.

* Phenolphthalein.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
P_2O_5	$Mg_2P_2O_7$	1.5676	0.6379	$PbSO_4$	$(PbCO_3)_2Pb(OH)_2$	0.8525	1.1731
P_2O_5	Na_2HPO_4	1.9995	0.5001	$PbSO_4$	PbO_2	0.7887	1.2679
P_2O_5	NaH_2PO_4	1.6900	0.5917	$PbSO_4$	Pb_3O_4	0.7535	1.3272
P_2O_5	$Na_2H_2P_2O_7$	1.5632	0.6397	$PbSO_4$	PbS	0.7889	1.2676
P_2O_5	$Na(NH_4)HPO_4 \cdot 4H_2O$	2.9452	0.3395				
P_2O_5*	Na_2O	0.8727	1.1458	Pd	K_2PdCl_6	3.7270	0.2683
P_2O_5	Na_3PO_4	2.3091	0.4331	Pd	$PdCl_2 \cdot 2H_2O$	2.0024	0.4994
P_2O_5	$(NH_4)_3PO_4(MoO_3)_{12}$	26.424	0.0378	Pd	PdI_2	3.3791	0.2959
				Pd	$Pd(NO_3)_2$	2.1623	0.4625
				Pd	HI	2.3970	0.4170
Pb	CH_3CO_2H	0.5797	1.7249	Pd	I	2.3790	0.4203
Pb	$Pb(C_2H_3O_2)_2$	1.5700	0.6369	PdI_2	HI	0.7096	1.4092
Pb	$PbCl_2$	1.3424	0.7449	PdI_2	I	0.7040	1.4204
Pb	$PbCO_3$	1.2897	0.7754				
Pb	$(PbCO_3)_2Pb(OH)_2$	1.2479	0.8014	Pt	K_2PtCl_6	2.4921	0.1609
Pb	$PbCrO_4$	1.5601	0.6410	Pt	$H_2PtCl_6 \cdot 6H_2O$	2.6558	0.3765
Pb	PbO	1.0773	0.9283	Pt	$(NH_4)_2PtCl_6$	2.2761	0.4393
Pb	PbO_2	1.1545	0.8662	Pt	$PtCl_4$	1.7266	0.5792
Pb	$Pb(OH)_2$	1.1643	0.8589	Pt	$PtCl_4 \cdot 5H_2O$	2.1881	0.4570
Pb	PbS	1.1549	0.8659	$PtCl_4$	K_2PtCl_6	1.4427	0.6931
Pb	$PbSO_4$	1.4639	0.6831	$PtCl_4$	$(NH_4)_2PtCl_6$	1.3177	0.7589
Pb	S	0.1548	6.4599	$PtCl_4 \cdot 5H_2O$	K_2PtCl_6	1.1383	0.8785
$PbCl_2$	Cl_2	0.2551	3.9202				
$PbCO_3$	CO_2	0.1547	6.0705	Pr	Pr_2O_3	1.1707	0.8542
$PbCrO_4$	Cr	0.1612	6.2034				
$PbCrO_4$	Cr_2O_3	0.2352	4.2531	Rh	Na_3RhCl_6	3.7382	0.2675
$PbCrO_4$	Na_2CrO_4	0.5014	1.9944	Rh	$RhCl_3$	2.0338	0.4917
$PbCrO_4$	Pb	0.6410	1.5600				
$PbCrO_4$	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	1.1733	0.8523	Rb	AgCl	1.6775	0.5961
				Rb	Cl	2.4098	0.4150
$PbCrO_4$	$(PbCO_3)_2Pb(OH)_2$	0.7996	1.2505	Rb	RbCl	1.4150	0.7067
				Rb	$RbCO_3$	1.3510	0.7402
$PbCrO_4$	PbO	0.6905	1.4482	Rb	Rb_2O	1.0937	0.9144
$PbCrO_4$	Pb_3O_4	0.7070	1.4142	Rb	Rb_2SO_4	1.5622	0.6402
$PbCrO_4$	$PbSO_4$	0.9383	1.0657	Rb	Rb_2PtCl_6	3.3862	0.2952
$PbMoO_4$	Pb	0.5642	1.7722	RbCl	AgCl	1.8550	0.8435
$PbMoO_4$	Mo	0.2615	3.8241	RbCl	Cl	0.2933	3.4098
$PbMoO_4$	MoO_3	0.3923	2.5491	Rb_2CO_3	$RbHCO_3$	1.2686	0.7883
PbO	$PbCl_2$	1.2461	0.8025	Rb_2O	RbCl	1.2939	0.7729
PbO	$PbCO_3$	1.1972	0.8353	Rb_2O	Rb_2SO_4	1.4284	0.7001
PbO	Pb	0.9283	1.0772	$RbPtCl_6$	RbCl	0.4178	2.3938
PbO	$PbCl_2$	1.2461	0.8025	$RbPtCl_6$	Rb_2CO_3	0.3987	2.5071
PbC	$PbCO_3$	1.1972	0.8353	$RbPtCl_6$	$RbHCO_3$	0.5060	1.9762
PbO	$Pb(NO_3)_2$	1.4842	0.6738	$RbPtCl_6$	Rb_2O	0.3229	3.0972
PbO	$PbSO_4$	1.3589	0.7359				
PbS	Pb	0.8659	1.1549	S	$BaSO_4$	7.2791	0.1374
PbS	PbO	0.9328	1.0720	S	H_2S	1.0629	0.9388
PbS	S	0.1341	7.4577	S	H_2SO_4	3.0585	0.3270
$PbSO_4$	$BaSO_4$	0.7700	1.2987	S	FeS	2.7412	0.3648
$PbSO_4$	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	1.2507	0.7995	S	FeS_2	1.8706	0.5346
				S	Na_2S	2.4344	0.4108
				S	Pb	6.4599	0.1548

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
S	SO_2	1.9978	0.5005	SiO_2	K_2SiF_6	3.6567	0.2735
S	SO_3	2.4967	0.4005	SiO_2	K_2SiO_3	2.5622	0.3903
SO_3	$BaSO_4$	3.6430	0.2745	SiO_2	SiF_4	1.7296	0.5782
SO_2	$Ca(HSO_3)_2$	1.5783	0.6336	SiO_2	SO_3	0.7727	1.2942
SO_2	H_2SO_3	1.2812	0.7805	SiO_2	$Si(OH)_4$	1.5975	0.6259
SO_2*	H_2SO_4	1.5309	0.6532	SiO_2	$ZnSiO_3$	2.3495	0.4256
SO_2†	H_2SO_4	0.7655	1.3064				
SO_2	$NaHSO_3$	1.6244	0.6156	Sn	Cl_2	0.5975	1.6771
SO_2	Na_2SO_3	1.9677	0.5082	Sn	$SnCl_2$	1.5974	0.6261
SO_2	$Na_2SO_3 \cdot 7H_2O$	3.9360	0.2541	Sn	$SnCl_2 \cdot 2H_2O$	1.7325	0.5772
SO_3	Al_2O_3	0.4255	2.3504	Sn	$SnCl_4$	2.1945	0.4555
SO_3	$Al_2(SO_4)_3$	1.4255	0.7015	Sn	SnO	1.1348	0.8812
SO_3	$BaSO_4$	2.9155	0.3430	Sn	SnO_2	1.2696	0.7877
SO_3	CaO	0.7003	1.4280	$SnCl_2$	Cl	0.3740	2.6738
SO_3	$CaSO_4$	1.7003	0.5881	$SnCl_2$	HCl	0.3847	2.6000
SO_3	H_2SO_4	1.2250	0.8163	$SnCl_2$	Fe_2O_3	1.0952	0.9130
SO_3	K_2SO_4	2.1765	0.4595	$SnCl_2$	$SnCl_2 \cdot 2H_2O$	1.0846	0.9221
SO_3	MgO(in $MgSO_4$)	0.5036	1.9859	$SnCl_4$	Cl	0.5444	1.8369
				$SnCl_4$	HCl	0.5568	1.7959
SO_3	$MgSO_4$	1.5036	0.6651	SnO_2	$SnCl_2 \cdot 2H_2O$	1.4974	0.6678
SO_3	$MnSO_4$	1.8858	0.5303	SnO_2	$SnCl_4$	1.7288	0.5784
SO_3	Na_2O	0.7743	1.2915	SnO_2	$SnCl_4$ $(NH_4Cl)_2$	2.4389	0.4100
SO_3	Na_2SO_4	1.7743	0.5636				
SO_3	66° O. V.	1.3146	0.7607	SnO_2	SnO	0.8938	1.1188
SO_3	$ZnSO_4$	2.0162	0.4960				
SO_4	$BaSO_4$	2.4298	0.4116	Sr	$SrCO_3$	1.6848	0.5935
$SO_3 \cdot HCl$	H_2SO_4	1.2625	0.7921	Sr	SrO	1.1826	0.8456
$S_2O_5Cl_2$	H_2SO_4	1.3683	0.7309	Sr	$SrSO_4$	2.0963	0.4770
				SrO	$SrCl_2$	1.5300	0.6536
Sb	$KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$	2.7649	0.3617	$SrSO_4$	SO_3	0.4357	2.2943
Sb	$SbCl_3$	1.8850	0.5305	Ta	$TaCl_5$	1.9767	0.5059
Sb	Sb_2O_3	1.1997	0.8336	Ta	Ta_2O_5	1.2162	0.8207
Sb	Sb_2O_5	1.3328	0.7503				
Sb	Sb_2S_3	1.4002	0.7142	Te	H_2TeO_4	1.5177	0.6587
Sb	Sb_2O_4	1.2662	0.7897	Te	$H_2TeO_4 2H_2O$	1.8003	0.5554
Sb_2O_3	Sb_2O_5	1.1109	0.9001	Te	TeO_2	1.2509	0.7994
Sb_2S_3	$SbCl_3$	1.3462	0.7428	Te	TeO_3	1.3765	0.7265
Se	H_2SeO_3	1.6315	0.6129	ThO_2	Th	0.8790	1.1379
Se	H_2SeO_4	1.8336	0.5454	ThO_2	$ThCl_4$	1.4155	0.7065
Se	SeO_2	1.4040	0.7123	ThO_2	$Th(NO_3)_4 \cdot 6H_2O$	2.2226	0.4492
Se	SeO_3	1.6060	0.6227				
Si	SiO_2	2.1307	0.4693	Ti	TiO_2	1.6652	0.6005
Si	SiO_3	1.2653	0.7903				
Si	SiO_4	1.5307	0.6533	Tl	TlCl	1.1738	0.8519
SiF_4	$BaSiF_6$	2.6814	0.3729	Tl	Tl_2CO_3	1.1470	0.8718
SiF_4	H_2SiF_6	1.3837	0.7227	Tl	TlI	1.622	0.6165
SiF_4	K_2SiF_6	2.1141	0.4730	Tl	$TlNO_3$	1.3040	0.7669
SiF_6	H_2SiF_6	1.0141	0.9860	Tl	Tl_2O	1.0392	0.9623
SiO_2	$BaSiF_6$	4.6380	0.2156	Tl_2CrO_4	Tl	0.7786	1.2843
SiO_2	H_2SiO_3	1.2988	0.7699	$TlHSO_4$	Tl	0.6775	1.4759

$A \times A' = B$ and $B \times B' = A$.

* Phenolphthalein. † Methyl Orange.

XVIII.—CONVERSION FACTORS (Continued)

A	B	A′	B′	A	B	A′	B′
TlI	Tl	0.6165	1.6222	WO_3	W	0.7931	1.2609
Tl_2PtCl_6	Tl	0.5000	1.9999	WO_3	$PbWO_4$	1.9610	0.5099
Tl_2PtCl_6	TlCl	0.5869	1.7038				
Tl_2PtCl_6	Tl_2CO_3	0.5738	1.7435	Zn	H_2SO_4	1.5004	0.6665
Tl_2PtCl_6	TlI	0.8111	1.2329	Zn	SO_3	1.4229	0.8164
Tl_2PtCl_6	$TlNO_3$	0.6520	1.5337	Zn	$ZnCl_2$	2.0849	0.4796
Tl_2PtCl_6	Tl_2O	0.5196	1.9244	Zn	ZnO	1.2448	0.8034
Tl_2PtCl_6	Tl_2SO_4	0.6178	1.6187	Zn	ZnP_2O_7	2.3309	0.4290
Tl_2SO_4	Tl	0.8094	1.6187	Zn	ZnS	1.4906	0.6709
				$ZnCl_2$	AgCl	2.1035	0.4754
UO_2	U	0.8817	1.1342	$ZnCl_2$	Cl	0.5204	1.9217
U_3O_8	U	0.8482	1.1789	$ZnCl_2$	NaCl	0.8579	1.1656
U_3O_8	UO_3	0.9621	1.0394	ZnO	H_2SO_4	1.2054	0.8296
U_3O_8	$UO_2(NO_3)_2 \cdot 6H_2O$	1.7876	0.5594	ZnO	SO_3	0.9840	1.0162
				ZnO	$ZnCl_2$	1.6749	0.5970
$U_2P_2O_{11}$	U	0.6671	1.4990	ZnO	$ZnCO_3$	1.5407	0.6490
$U_2P_2O_{11}$	UO_3	0.7566	1.3216	ZnO	ZnP_2O_7	1.8726	0.5340
				ZnO	ZnS	1.1975	0.8351
V_2O_4	V	0.6024	1.6276	ZnO	$ZnSO_4$	1.9840	0.5040
V_2O_5	V	0.5604	1.7843	ZnO	$ZnSO_4 \cdot 7H_2O$	3.5340	0.2830
V_2O_5	VO_4	1.2638	0.7913	ZnS	$BaSO_4$	2.3957	0.4174
				ZnS	$ZnSO_4 \cdot 7H_2O$	2.9510	0.3389
Yb_2O_3	Yb	0.8775	1.1396	$ZnSiO_3$	SiO_2	0.4250	2.3495
Y_2O_3	Y	0.7876	1.2697	$ZnSO_4$	SO_3	0.4960	2.0162
W	$PbWO_4$	3.4477	0.2900	ZrO_2	Zr	0.7390	1.3532
WO_3	W	0.8519	1.1739				

$A \times A' = B$ and $B \times B' = A$.

NOTE.—The editor will welcome additional factors not appearing in these tables. A number of factors appearing in this list were taken from Van Nostrand's Chemical Annual. Olsen. 1913.

Example of Method for Using Factors. Suppose the product weighed is 0.8535 gram AgCl and the equivalent weight of Cl is desired; hunt up the factors AgCl–Cl. This may be found on the first page of the conversion factors, a little below the middle of the page. Using the formula $A \times A' = B$, and substituting the values for A (weight of AgCl) and A' (factor) we have $0.8535 \times 0.2474 = 0.21124$ gram Cl. If on the other hand, the weight of Cl were known to be, say, 0.2501 gram and the weight of the equivalent AgCl were desired, we would use the formula $B \times B' = A$ and, substituting the values for B and B', we would have $0.2501 \times 4.0423 = 1.01098$ gram AgCl.

XIX.—COMPARISON OF CENTIGRADE AND FAHRENHEIT SCA

° C.	−100	−0	+0	+100	+200	+300	+400	+500	+600	+700	+800	+900
	°F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.
0	−148	+ 32	32	+212	392	572	752	932	1112	1292	1472	165
5	−157	+ 23	41	221	401	581	761	941	1121	1301	1481	166
10	−166	+ 14	50	230	410	590	770	950	1130	1310	1490	167
15	−175	+ 5	59	239	419	599	779	959	1139	1319	1499	167
20	−184	− 4	68	248	428	608	788	968	1148	1328	1508	168
25	−193	− 13	77	257	437	617	797	977	1157	1337	1517	169
30	−202	− 22	86	266	446	626	806	986	1166	1346	1526	170
35	−211	− 31	95	275	455	635	815	995	1175	1355	1535	171
40	−220	− 40	104	284	464	644	824	1004	1184	1364	1544	172
45	−229	− 49	113	293	473	653	833	1013	1193	1373	1553	173
50	−238	− 58	122	302	482	662	842	1022	1202	1382	1562	174
55	−247	− 67	131	311	491	671	851	1031	1211	1391	1571	175
60	−256	− 76	140	320	500	680	860	1040	1220	1400	1580	176
65	−265	− 85	149	329	509	689	869	1049	1229	1409	1589	176
70	−274	− 94	158	338	518	698	878	1058	1238	1418	1598	177
75	−283	−103	167	347	527	707	887	1067	1247	1427	1607	178
80	−292	−112	176	356	536	716	896	1076	1256	1436	1616	179
85	−301	−121	185	365	545	725	905	1085	1265	1445	1625	180
90	−310	−130	194	374	554	734	914	1094	1274	1454	1634	181
95	−319	−139	203	383	563	743	923	1103	1283	1463	1643	182
100	−328	−148	+212	392	572	752	932	1112	1292	1472	1652	183

° C.	−200	−100	+100	+200	+300	+400	+500	+600	+700	+800	+900	+1000

C°	1100	1200	1300	1400	1500	1600	1700	1800	1900	2
F°	2012	2192	2372	2552	2732	2912	3092	3272	3452	3

Degrees C. × 1.8 + 32 = Degrees F. Degrees F. − 32 ÷ 1.8 = Degrees

Absolute zero, −273° C. = −459° F.

Comparison of Centigrade and Fahrenheit Scale for Every 1° C. fro 0° to 100° C.

C.	0	10	20	30	40	50	60	70	80	90
	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.
0	32	50	68	86	104	122	140	158	176	194
1	33.8	51.8	69.8	87.8	105.8	123.8	141.8	159.8	177.8	195.8
2	35.6	53.6	71.6	89.6	107.6	125.6	143.6	161.6	179.6	197.6
3	37.4	55.4	73.4	91.4	109.4	127.4	145.4	163.4	181.4	199.4
4	39.2	57.2	75.2	93.2	111.2	129.2	147.2	165.2	183.2	201.2
5	41.0	59	77	95	113	131	149	167	185	203
6	42.8	60.8	78.8	96.8	114.8	132.8	150.8	168.8	186.8	204.8
7	44.6	62.6	80.6	98.6	116.6	134.6	152.6	170.6	188.6	206.6
8	46.4	64.4	82.4	100.4	118.4	136.4	154.4	172.4	190.4	208.4
9	48.2	66.2	84.2	102.2	120.2	138.2	156.2	174.2	192.2	210.2
C.	9	19	29	39	49	59	69	79	89	99

100° C. = 212° F.

XX.—RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY AND THE WEIGHT OF ONE UNITED STATES GALLON AT 60° F.

Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.
10	1.0000	8.33	31	0.8695	7.24	52	0.7692	6.41	73	0.6896	5.75
11	0.9929	8.27	32	0.8641	7.20	53	0.7650	6.37	74	0.6863	5.52
12	0.9859	8.21	33	0.8588	7.15	54	0.7608	6.34	75	0.6829	5.69
13	0.9790	8.16	34	0.8536	7.11	55	0.7567	6.30	76	0.6796	5.66
14	0.9722	8.10	35	0.8484	7.07	56	0.7526	6.27	77	0.6763	5.63
15	0.9655	8.04	36	0.8433	7.03	57	0.7486	6.24	78	0.6730	5.60
16	0.9589	7.99	37	0.8383	6.98	58	0.7446	6.20	79	0.6698	5.58
17	0.9523	7.93	38	0.8333	6.94	59	0.7407	6.17	80	0.6666	5.55
18	0.9459	7.88	39	0.8284	6.90	60	0.7368	6.14	81	0.6635	5.52
19	0.9395	7.83	40	0.8235	6.86	61	0.7329	6.11	82	0.6604	5.50
20	0.9333	7.78	41	0.8187	6.82	62	0.7290	6.07	83	0.6573	5.48
21	0.9271	7.72	42	0.8139	6.78	63	0.7253	6.04	84	0.6542	5.45
22	0.9210	7.67	43	0.8092	6.74	64	0.7216	6.01	85	0.6511	5.42
23	0.9150	7.62	44	0.8045	6.70	65	0.7179	5.98	86	0.6481	5.40
24	0.9090	7.57	45	0.8000	6.66	66	0.7142	5.95	87	0.6451	5.38
25	0.9032	7.53	46	0.7954	6.63	67	0.7106	5.92	88	0.6422	5.36
26	0.8974	7.48	47	0.7909	6.59	68	0.7070	5.89	89	0.6392	5.33
27	0.8917	7.43	48	0.7865	6.55	69	0.7035	5.86	90	0.6363	5.30
28	0.8860	7.38	49	0.7821	6.52	70	0.7000	5.83	95	0.6222	5.18
29	0.8805	7.34	50	0.7777	6.48	71	0.6965	5.80	..	.....	...
30	0.8750	7.29	51	0.7734	6.44	72	0.6930	5.78	..	.....	...

VOLUMETRIC FACTORS

1 cc. N/2 HCl = .018185 gram HCl.
1 cc. N/10HCl = .003637 gram HCl.
1 cc. N/2 KOH = .028 gram KOH.
1 cc. N/6 KOH = .047 gram oleic acid = .008133 gram H_2SO_4.
1 cc. N/10 KOH = .0056 gram KOH.
1 cc. $K_2Cr_2O_7$ 3.8633 gram per liter = .0038633 gram $K_2Cr_2O_7$ = .010 gram I.
1 cc. N/10 $Na_2S_2O_3+5H_2O$ = .0248 gram $Na_2S_2O_3+5H_2O$ = .01265 gram I.

XXI.—COMPARISON OF METRIC AND CUSTOMARY UNITS (U. S.).

Length

1 millimeter, mm.	=0.03937 inch.	1 inch	=25.4001 millimeters.
1 centimeter, cm.	=0.39371 inch.	1 inch	= 2.54001 centimeters.
1 meter, m.	=3.28083 feet.	1 foot	= 0.304801 meter.
1 meter	=1.09361 yards.	1 yard	= 0.914402 meter.
1 kilometer	=0.62137 (U. S.) mile.	1 mile	= 1.60935 kilometers.

Areas

1 square millimeter, sq.mm.	= 0.00155 sq.in.	1 sq.in.	=645.16 sq.mm.
1 square centimeter, sq.cm.	= 0.1550 sq.in.	1 sq.in.	= 6.452 sq.cm.
1 square meter, sq.m.	=10.764 sq.ft.	1 sq.ft.	= 0.0929 sq.m.
1 square meter	= 1.196 sq.yd.	1 sq.yd.	= 0.8361 sq.m.
1 square kilometers	= 0.3861 sq.mi.	1 sq.mi.	= 2.5900 sq.km.
1 hectare	= 2.471 acres.	1 acre	= 0.4047 hectare.

Volumes

1 cubic millimeter, cu.mm.	= 0.000061 in.	1 cu.in.	=16,387.2 cu.mm.
1 cubic centimeter, cc.	= 0.06103 cu.in.	1 cu.in.	=16.3872 cc.
1 cubic meter	=35.314 cu.ft.	1 cu.ft.	= 0.02832 cu.m.
	=61,028 cu.ins.		=28.32 liters.
1 cubic meter	= 1.3079 cu.yd.	1 cu.yd.	= 0.7645 cu.m.

Capacities

1 cubic centimeter, cc.	=0.03381 (U.S.) liquid ounce.	1 ounce	=29.574 cc.
1 cubic centimeter	=0.2705 (U. S.) apothecaries' dram.	1 dram	=3.6967 cc.
1 cubic centimeter	=0.8115 (U. S.) apothecaries' scruple.	1 scruple	=1.2322 cc.
1 liter	=1.05668 (U. S.) liquid quarts.	1 quart	=0.94636 liter.
1 liter	=0.26417 (U. S.) gallon.	1 gallon	=3.78543 liters.
1 liter	=0.11351 (U. S.) peck.	1 peck	=8.80982 liters.
1 hectoliter	=2.83774 (U. S.) bushels.	1 bushel	=0.35239 hectoliter.

Masses

1 gram	=15.4324 grains.	1 grain	= 0.06480 gram.
1 gram	= 0.03527 avoirdupois ounce.	1 ounce (av.)	=28.3495 grams.
1 gram	= 0.03215 troy ounce.	1 ounce (troy)	=31.10348 grams.
1 kilogram	= 2.20462 pounds (av.)	1 pound (av.)	= 0.45359 kilogram.
1 kilogram	= 2.67923 pounds (troy).	1 pound (troy)	= 0.37324 kilogram.

Table of Equivalents, U. S. Bureau of Standards. For British Imperial Weights and Measures see Van Nostrand's Chemical Annual.

Avoirdupois Weight

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams	=1 ounce	= 28.35 grams.
16 ounces	=1 pound	=453.59 grams.
25 pounds	=1 quarter	= 11.34 kilograms.
4 quarters	=1 hundred weight	= 45.359 kilograms.

1 avoirdupois pound contains 7000 grains.
1 avoirdupois ounce contains 437.5 grains.

Apothecaries' Weight

The system of weights employed in weighing medicines.

1 grain		=	0.0648 gram.
20 grains	= 1 scruple	=	1.296 grams.
3 scruples	= 1 drachm	=	3.888 grams.
8 drachms	= 1 ounce	=	31.103 grams.
12 ounces	= 1 pound	=	373.236 grams.

1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.

Fluid Measure

1 minim		=	.06161	cubic centimeter.
60 minims	= 1 fluid drachm	=	3.696	cubic centimeters.
8 fluid drachms	= 1 fluid ounce	=	29.573	cubic centimeters.
16 fluid ounces	= 1 pint	=	473.179	cubic centimeters.
8 pints	= 1 gallon	=	3.785	liters.

1 gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures employed by apothecaries.

XXII.—A TABLE OF CONSTANTS

THE UNITED GAS

All Volumes of Gases and Vapors are given at 60° F. and 30″ pressure.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
NAME OF GAS OR VAPOR.	SYMBOL OR FORMULA.	Molecular Weight.	Sp. Gravity Gas or Vapor at 60° F. Air = 1.0.	Boiling-point ° Fahr.	Sp. Gravity Liquid at 60° F. Water = 1.0.	Sp. Heat Eq. Wts. at Const. Pr. Water = 1.0.	Cubic Feet per Pound.	Weight 1 Cubic Foot in Pounds.	Heat of Combustion. Calories per Molecular Wt. in Grams.	Heat of Combustion. British Thermal Units. Per Cu. Ft.	Heat of Combustion. British Thermal Units. Per Pound.
Carbon to CO	C	12	0.8292	.....	.....	.....	15.749	.06350	29.000	276.2	4.250
Carbon to CO_2	C	12	0.8292	.....	.....	.....	15.749	.06350	96.960	923.5	14.544
Carbonic Ox...	CO	28	0.9671	.....	.....	0.2450	13.503	.07407	67.960	323.5	4.388
Hydrogen....	H	1	0.0692	.....	.....	3.0490	188.620	.00530	68.360	326.2	61.523
Methane.....	Paraffin Series C_nH_{2n+2} CH_4	16	0.5529	.....	.....	0.5929	23.626	.04234	211.930	1009.0	23.839
Ethane.....	Paraffin Series C_nH_{2n+2} C_2H_6	30	1.0368	.....	.....	.....	12.594	.07940	370.440	1764.4	22.226
Propane.....	Paraffin Series C_nH_{2n+2} C_3H_8	44	1.5206	− 13°	.....	.....	8.587	.11645	529.210	2521.0	21.651
Butane.....	Paraffin Series C_nH_{2n+2} C_4H_{10}	58	2.0045	+ 33°	.....	.....	6.514	.15350	687.190	3274.0	21.326
Pentane.....	Paraffin Series C_nH_{2n+2} C_5H_{12}	72	2.4883	+100°	0.6273	.....	5.248	.19055	847.110	4035.6	21.177
Hexane.....	Paraffin Series C_nH_{2n+2} C_6H_{14}	86	2.9721	+156°	0.6640	.....	4.393	.22760	999.200	4759.8	20.914
Ethylene....	Olefin Series C_nH_{2n} C_2H_4	28	0.9676	.....	.....	0.4040	13.495	.07410	333.350	1588.0	21.430
Propylene....	Olefin Series C_nH_{2n} C_3H_6	42	1.4514	.....	.....	.....	8.997	.11115	492.740	2347.2	21.120
Butylene.....	Olefin Series C_nH_{2n} C_4H_8	56	1.9353	+ 23°	.....	.....	6.747	.14820	650.620	3099.2	20.913
Amylene.....	Olefin Series C_nH_{2n} C_5H_{10}	70	2.4191	+102°	0.6511	.....	5.398	.18525	807.630	3847.2	20.767
Acetylene....	Acetyl. Series C_nH_{2n-2} C_2H_2	26	0.8984	.....	.....	.....	14.534	.06880	310.050	1476.7	21.465
Allylene.....	Acetyl. Series C_nH_{2n-2} C_3H_4	40	1.3823	.....	.....	.....	9.447	.10585	467.550	2227.1	21.040
Crotonylene..	Acetyl. Series C_nH_{2n-2} C_4H_6	54	1.8661	+ 64°	.....	.....	6.998	.14290	.....	.....	.....
Benzene.....	Aromat. Series C_nH_{2n-6} C_6H_6	78	2.6953	+177°	0.8846	0.3754	4.845	.20640	799.350	3807.5	18.447
Toluene.....	Aromat. Series C_nH_{2n-6} C_7H_8	92	3.1792	+230°	0.8720	.....	4.107	.24345	955.680	4552.0	18.699
Xylene.....	Aromat. Series C_nH_{2n-6} C_8H_{10}	106	3.6630	+287°	0.8692	.....	3.565	.28050	.....	.....	.....
Mesitylene....	Aromat. Series C_nH_{2n-6} C_9H_{12}	120	4.1468	+326°	.....	.....	3.149	.31755	1,282.310	6108.0	19.235
Naphthalene..	$C_{10}H_8$	128	4.4230	+424.4°	1.1517		2.952	.33870	.....	.....	.....
Hydrogen Sul.	H_2S	34	1.1769	.....	.....	0.2423	11.096	.09012	140.900	672.2	7.549
Ammonia.....	NH_3	17	0.5888	.....	.....	0.5083	22.178	.04509	90.560	432.8	9.598
Hydrocy. acid.	HCN	27	0.9348	.....	.....	.....	13.968	.07159	158.620	757.0	10.573
Cyanogen....	C_2N_2	52	1.8000	.....	.....	.....	7.258	.13779	259.620	1238.2	8.986
Carbon Bi-Sul.	CS_2	76	2.6298	+114.8°	.....	.....	4.965	.20139	265.130	1264.6	6.279
Methyl Alc....	CH_4O	32	1.1121	+131.2°	0.8027	.....	11.742	.08516	182.230	872.9	10.250
Ethyl Alcohol.	C_2H_6O	46	1.5894	+172.9°	0.7946	1.4534	8.216	.12172	340.530	1622.0	13.325
Carbonic Acid.	CO_2	44	1.5195	.....	.....	0.2163	8.593	.11637	.....	.....	.....
Water.....	H_2O	18	0.6217	+ 212°	1.0000	0.4805	21.004	.04761	.....	.....	.....
Sulphur Diox.	SO_2	64	2.2128	.....	.....	0.1553	5.901	.16945	.....	.....	.....
Oxygen.....	O	16	1.1052	.....	.....	0.2174	11.816	.08463	.....	.....	.....
Nitrogen.....	N	14	0.9701	.....	.....	0.2438	13.460	.07429	.....	.....	.....
Air.....	.....	..	1.0000	.....	.....	0.2374	13.059	.07658	.....	.....	.....

AUTHORITIES AND METH

In Column IX. the figures given in Hempel's "Gas Analysis," p. 375, were selected for the fundamental weight of Oxygen, Nitrogen, Hydrogen, Carbonic Oxide and Air.

The formula used for the conversion to English units, is—grams per liter at 0° C. and 760 mm. × .05922 = pounds per cu.ft. at 60° F. and 30″ pressure. The derivation of the factor employed is

$$.05922 = \frac{28.316 \times .0022046 \times 30.00 \times 492}{29.92 \times 520}.$$

The weights of the compound gases are calculated from these data by Avogadro's law.

Column IV. is calculated by the formula: $\text{sp.gr} = \frac{\text{wt. 1 cu. ft. gas}}{\text{wt. 1 cu.ft. air}}$, and the figures thus obtained agree with the theoretical formula: $\text{sp.gr.} = \frac{\text{mol. wt.}}{28.94}$.

OR CERTAIN GASES AND VAPORS

MPROVEMENT COMPANY

The Temperature of Products of Combustion is reduced to 18° C. = 64.4° F.

XIII.	XIV.	XV.	XVI.	XVII.	XVIII	XIX.	XX.	XXI.	XXII.	XXIII.	XXIV.	XXV.	XXVI.
Cu. Ft. per Cu. Ft. of Combustible.					Pounds per Pound of Combustible.					Heat of Formation at Const. Pres.			
Req. for Combustion.		Products of Combustion.			Req. for Combustion.		Products of Combustion.			Calories per Molecular Wt. in Grams.	B.t.u.		NAME OF GAS OR VAPOR.
Air.	Oxygen.	CO_2	H_2O		Air	Oxygen.	CO_2	H_2O			Per Cu. Ft.	Per Pound.	
4.785	1.0	..	...	CO—2.0	5 771	1.333+	.....	...	CO—2.333+	.....	.....	.....	Carbon to CO
9.570	2.0	2.0	..	.....	11.541	2.666+	3.666+	...	.....	.....	.....	.....	Carbon to CO_2
2.393	0.5	1.0	..	.....	2.471	.571	1.571	...	.....	.....	+138.4	+1869.2	Carbonic Ox.
2.393	0.5	..	1.0	.....	34.624	8.000	.....	9.000	.....	.....	.....	.....	Hydrogen
9.570	2.0	1.0	2.0	.....	17.312	4.000	2.750	2.250	.....	+21,750	+103.1	+2435.6	Methane
16.748	3.5	2.0	3.0	.....	16.156	3.733	2.933	1.800	.....	+28,560	+136.0	+1713.6	Ethane
23.925	5.0	3.0	4.0	.....	15.737	3.636	3.000	1.636	.....	+35,110	+167.2	+1436.3	Propane
31.103	6.5	4.0	5.0	.....	15.520	3.586	3.034	1.552	.....	+42,450	+202.2	+1317.3	Butane
38.280	8.0	5.0	6.0	.....	15.386	3.555	3.055	1.500	.....	+47,850	+227.9	+1196.2	Pentane
45.458	9.5	6.0	7.0	.....	15.295	3.534	3.069	1.465	.....	+61,080	+290.9	+1278.4	Hexane
14.355	3.0	2.0	2.0	.....	14.836	3.428	3.142	1.286	.....	−2,710	−12.9	−174.2	Ethylene
21.533	4.5	3.0	3.0	.....	14.836	3.428	3.142	1.286	.....	+3,220	+15.3	+138.1	Propylene
28.710	6.0	4.0	4.0	.....	14.836	3.428	3.142	1.286	.....	+10,660	+50.7	+342.6	Butylene
35.888	7.5	5.0	5.0	.....	14.836	3.428	3.142	1.286	.....	+18,970	+113.7	+614.1	Amylene
11.963	2.5	2.0	1.0	.....	13.313	3.076	3.384	0.692	.....	−47,770	−227.5	−3300.7	Acetylene
19.140	4.0	3.0	2.0	.....	13.850	3.200	3.300	0.900	.....	−39,650	−188.8	−1784.2	Allylene
26.318	5.5	4.0	3.0	.....	14.105	3.259	3.259	1.300	.....	.....	.....	.....	Crotonylene
35.888	7.5	6.0	3.0	.....	13.313	3.076	3.384	0.692	.....	−12,510	−47.3	−229.3	Benzene
43.065	9.0	7.0	4.0	.....	13.547	3.130	3.348	0.782	.....	−3,520	+16.7	−68.8	Toluene
50.243	10.5	8.0	5.0	.....	13.720	3.170	3.311	0.849	.....	.....	.....	.....	Xylene
57.420	12.0	9.0	6.0	.....	13.850	3.200	3.300	0.900	.....	+490	+2.3	+7.3	Mesitylene
57.420	12.0	10.0	4.0	.....	12.984	3.000	3.437	0.563	.....	.....	.....	.....	Naphthalene
7.178	1.5	..	1.0	SO_2—1.0	6.111	1.412	.....	0.529	SO_2—1.883	+4,740	+22.6	+250.9	Hydrogen Sul.
3.589	0.75	..	1.5	N—0.5	6.111	1.412	.....	1.588	N—0.823	+11,890	+56.7	+1259.0	Ammonia
5.981	1.25	1.0	0.5	N—0.5	6.410	1.481	1.630	0.333	N—0.518	−27,480	−131.1	−1832.0	Hydrocy. acid
9.570	2.0	2.0	..	N—1.0	5.323	1.230	1.692	...	N—0.538	−65,700	−313.2	−2273.9	Cyanogen
14.355	3.0	1.0	..	SO_2—2.0	5.466	1.263	0.579	...	SO_2—1.684	−26,010	−124.0	−616.0	Carbon Bi-Sul.
7.178	1.5	1.0	2.0	.....	6.492	1.500	1.375	1.125	.....	+51,450	+246.4	+2894.0	Methyl Alc.
14.355	3.0	2.0	3.0	.....	9.033	2.087	1.913	1.174	.....	+58,470	+278.5	+2288.0	Ethyl Alcohol.
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	+463.1	+3979.1	Carbonic Acid
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	+327.1	+6870.4	Water
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	+337.3	+1999.1	Sulphur Diox.
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Oxygen
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Nitrogen
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	Air

ODS OF CALCULATION.

Columns V. and VI. are taken chiefly from Lunge's "Coal Tar and Ammonia."

Column VII. is from Ganot's "Physics," edition 1896, page 445.

Column X. and XXIII. are from Julius Thomsen's "Thermochemical Investigations," and his results are translated into English units in columns XI.–XII. and XXIV.–XXV.

Columns XIII. and XVIII. are calculated on the assumption that

air = 20.9% oxygen + 79.1% nitrogen by *Volume*.

air = 23.13% oxygen + 76.87% nitrogen *by Weight*.

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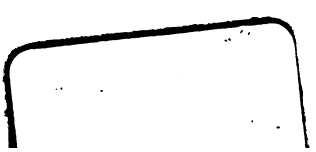
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